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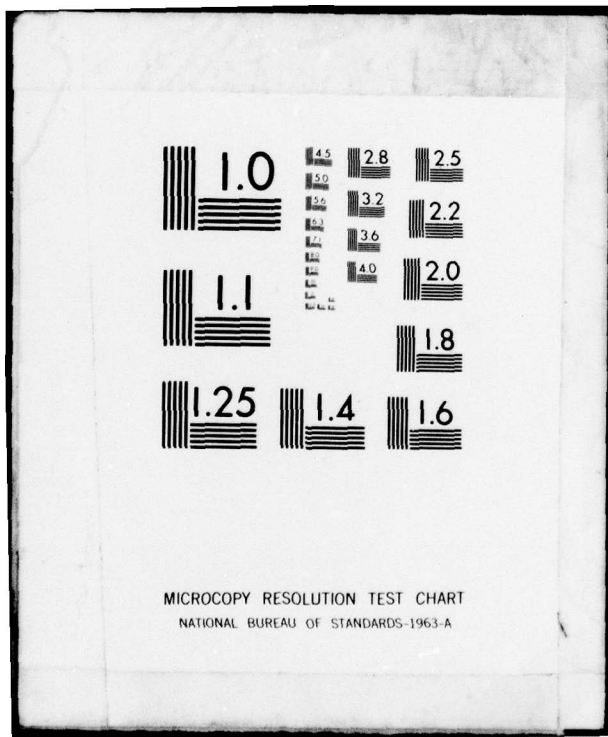
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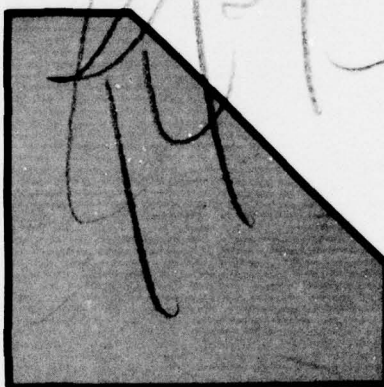
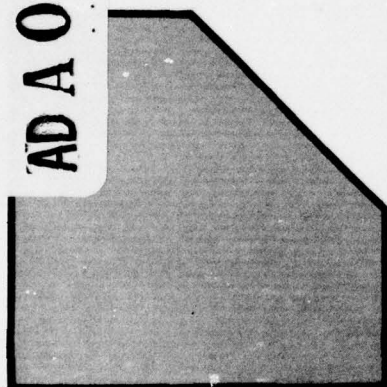
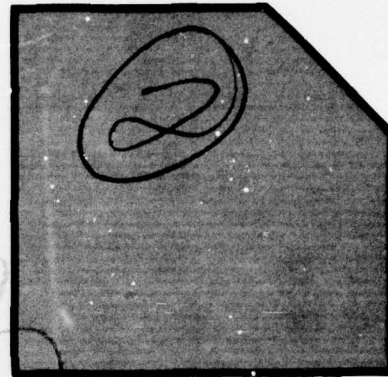
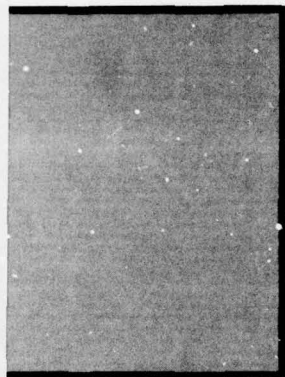
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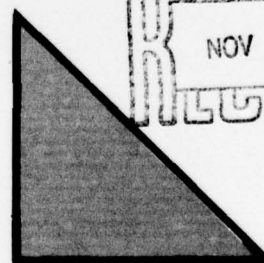
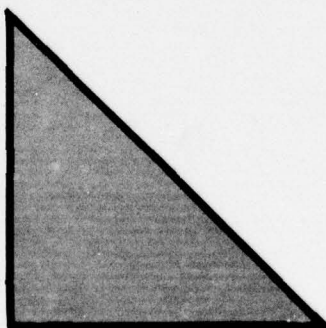
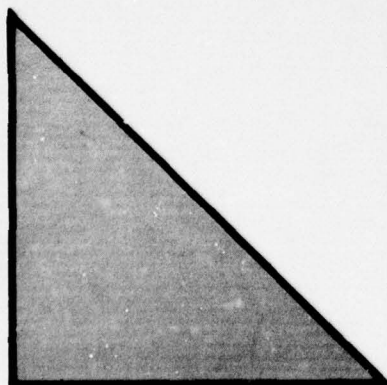
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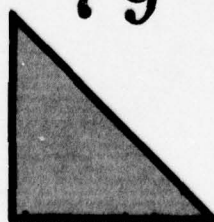
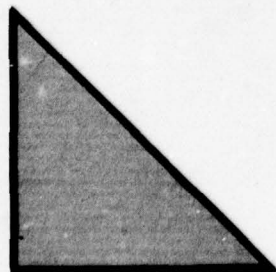


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TUTORIAL ON CORROSION,
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(Abstract and text were not provided for publication)

AN OVERVIEW OF MATERIALS SCIENCE TODAY IN RELATION TO THE MATERIALS WORLD

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ABSTRACT

Materials science can be classified into three broad categories to facilitate discussing it in relation to the cycle of materials use. These categories are Materials Transformation Science, Materials Structure/Property Science, and Materials Durability Science. Discussion of the relation of materials science to the cycle of materials use usually takes place in a U. S. national context.

Recently many aspects of this relationship were discussed in an international context by persons from thirty-four countries and summarized in workshop reports. An analysis of the main results in the light of current themes in materials science will be presented.

Today I would like to present a broad prospectus of current trends in the relation of materials science and engineering to economic and policy concerns. This is an enormous subject. There is a great deal of activity at the national level. Slide 1. This slide and the next one give a partial listing of current reviews or similar overviews. I have put two activities of the National Academies first because I think they offer a useful basis for a broad perspective talk.

The National Materials Advisory Board has compiled a list of ten critical issues in materials. This list provides a good framework for my talk. I will go through their list illustrating it with examples from the other sources listed on these slides. I am going to emphasize examples from the International Materials Congress. You are probably more familiar with our domestic materials activities and I think some foreign viewpoints will be of most interest.

The Congressional agencies have extensive policy-oriented materials programs. These are very wide-ranging but can perhaps be typified by two features. First, an attempt to identify and analyze materials problems which have national significance. Second, a concern with how the Government deals with these problems, including how effectively its resources are coordinated and utilized.

A good overview of the activities of these three Congressional agencies is given in the Proceedings of the 1978 Henniker Conference on National Materials Policy.

The Executive Branch agencies, Slide 2, have a wide range of studies on the technical and technical-policy interface in relation to materials. The Committee on Materials, so-called "COMAT," has just completed an inventory of materials research in industry which supplements their recent inventory of materials research funded by the Federal Government. The Department of Energy has a wide range of studies underway; I think three are especially noteworthy: the Coal Conversion Materials Workshops which are held every Fall at the National Bureau of Standards, the recent Solar Energy Materials Workshop whose proceedings are about to be published, and the Materials Council Workshops run by

the Division of Basic Energy Sciences. The recent one on Ceramics is certainly an excellent summary of the kinds of long-range research pertinent to the application of ceramics in energy technologies. NIH and EPA in responding to their responsibilities under the Toxic Substances Control Act have established a Chemical Information System which includes information such as standard x-ray patterns of great interest for materials identification in general, as well as the identification of toxic substances. The Department of Transportation recently held a conference on Advanced Automotive Technology. Of the three workshops one concentrated on structures and materials. This proceedings will be very interesting when it is issued. The Department of Defense has, of course, many materials activities but I would like to mention especially the Defense Advanced Research Projects Agency and its materials program which has been summarized in an excellent overview talk by its Director, Dr. Arden Bement. The National Science Foundation is, of course, the largest single supporter of basic scientific research in materials, and every year sponsors a series of workshops on selected topics which it believes to be of greatest interest. I understand that they are currently considering some such activity on materials substitution. The National Bureau of Standards program on materials focuses on the science underlying materials processing, structure/property relationship, and materials durability. It is a measurement- and data-oriented program. The Department of Interior has a strong materials program related to mining and extractive metallurgy in particular. They also chair the Committee on Materials.

A unique activity in the materials field and one of great interest is the Domestic Minerals Policy Review undertaken at the direction of the President. This review deals with the issue of materials supply and all of the manifold implications. Unfortunately, it has not been released so that I cannot quote any results from it.

The materials societies of this country play, of course, an important role including such societies as the Chemical Society which is not thought of as being primarily a materials society but has strong materials interests. Let me content myself with one example in this field. The Federation of Materials Societies, an umbrella organization of some fifteen materials societies, runs a national conference on materials policy every two years and the proceedings are of prime reference to the materials policy interface.

One approach to a materials overview talk would be to attempt a brief summary of each of the programs listed on the last two slides. I prefer instead to try to go through in terms of the ten critical issues in materials, as defined by the National Materials Advisory Board, picking out examples from the work of these various agencies to illustrate them in some cases, but attempting when possible to pick non-U.S. examples because I think they will be of most interest to you.

Slide 3 lists the first three of the ten most critical issues in materials as developed by the National Materials Advisory Board. I want to walk through these ten issues simply giving you the title of each at this point. I will then come back, describe each issue in a little more detail, and give examples of pertinent activities. The first three issues all concern innovation in the materials field and the processing of materials. The first issue is the adequacy of materials processing research as opposed to research on other parts of the cycle of materials use. The second issue is the adequacy of long-term research as opposed to the shorter range research to solve immediate problems. The third issue concerns the alleged need for better cooperation between indus-

try, government, and universities in research and development to meet foreign competition where, in some cases, the cooperation is very good.

Slide 4. The next two issues concern materials in relation to energy. As defined by NMAB, these two are the question of the energy required to produce materials and the consideration of and reduction of these costs when possible. The second concerns the effectiveness of Federal support mechanisms in developing improved energy conversion technologies such as nuclear power or coal gasification or solar energy. The next pair of issues concern health, safety, and the environment. The first concerns the need for better methods to detoxify materials, store, or dispose of them. The second concerns the need for better comparative assessment of the risks associated with the processing and use of materials.

Slide 5. Finally, the last three critical issues concern supply, recycling, and materials availability in general. The first is the issue of the potential for conservation in the use of materials and is one of the issues under which the question of corrosion abatement and lifetime extension comes up. The ninth issue is the need for and the question of whether it is possible to have improved predictive capability for supply and demand of materials. The tenth is the issue of what options there are for reducing our import dependence in addition to the ones already covered under the first nine issues.

Slide 6. Let's turn now to the first issue in somewhat more detail. The Board stated that, "More emphasis on materials processing research is needed, especially research on innovative processing techniques that would result in major improvements in productivity rather than marginal development of existing processes. While much effort has been expended on materials properties research, there appears to be a lack of research on the methods of producing and forming materials to give the uniform, high property values necessary for reproducible, high performance products. As a result, materials processing improvements are often only of an incremental nature and without major significance. To cite only two examples, after years of modest advances major new technology is now needed, both to extract the metal values from low-grade ores and to reduce metal removal (machining) costs. Productivity in materials processing must be enhanced by such improvements if the U.S. is to remain an effective competitor among manufacturing nations."

I am sure the members of the National Materials Advisory Board were well aware of such exciting and active fields as rapid solidification, or laser processing, or thixocasting and rheocasting. The Board surely did not mean to imply that there is no activity in innovative fields but rather that such activity is the exception and that more effort is needed in these areas and to find and support additional areas, including the very important area of processing materials from low-grade ores.

Slide 7. In this connection, the results of a workshop held in March at the International Materials Congress are of interest. There were ten workshops at that conference, one of which dealt with materials science and technology for more efficient mining, processing, and recycling. In the area of mining the workshop drew attention to the overriding concern with economics rather than with energy efficiency in mining but noted that improvements in energy efficiency are possible. In capsule form, their conclusions are indicated on Slide 7. The workshop suggested that selective mining of the most concentrated areas of an ore body is a promising technique, but that it requires improved remote sensing and capability for *in situ* analysis to determine where these most promising areas for selected mining are located. Another approach is to use in-mine preconcentration so that the energy costs associated with moving the full weight of the

rock are reduced since only the concentrate need be removed. Also, the remaining material can be used to backfill the mine and reduce the problem of mining waste disposal. Another area is that of giving increased attention to retreat mining by robbing the supporting pillars in worked-out areas accompanied by backfilling with the mining and processing wastes to minimize subsidence of the surface. Finally, the whole topic of automated mining, including remote sensing and control, is very promising for use with thin seams and in hazardous conditions.

Slide 8. On the subject of beneficiation, Dr. Newnham of Australia used figures developed by Battelle to analyze the possibility for energy savings in this stage of the process for aluminum, cement, lead, zinc, or copper. His conclusions stand out from this slide, that the principal opportunities are in the comminution, that is the grinding of cement and copper ore and in the flotation of copper ore. In any case, the potential savings though significant are still a relatively small fraction of the total energy required to produce the finished material except in the case of copper where, as you might expect from the use of low-grade ore, comminution is a substantial fraction of the total energy required.

Slide 9. Dr. Newnham went on to describe an approach being followed by the Australian Mining Energy Association. Essentially this program aims at tailoring the primary mining itself to the production of ore of controlled characteristics. That is, the drilling and blasting should be carried out to produce and optimal size rock to reduce the subsequent comminution energy required. To do this they are coupling programs on seismic measurement to get more accurate prediction of the fragmentation characteristics of the rock to be broken up with better modeling of large volume explosive fragmentation effects. Combining these two they hope to be able to tailor the mining to the particular ore characteristics.

Slide 10. Another non-U.S. viewpoint is summarized in this slide on the Finnish program in grinding and classification. Professor Laurila of the Academy of Finland points out that energy used in comminution is generally electrical energy and therefore savings in this type of energy are more important than a simple percentage value based on total energy might indicate. He estimates that industrial grinding processes consumes the order of three to four percent of the total electrical energy developed in the whole world and that cement alone requires close to one percent of the total world electrical energy. He ranks the others in order of importance as the grinding of wood, iron ores, coal, non-ferrous ores, and wheat. The Finnish program is directing attention toward the optimum distribution of particle sizes which is needed for subsequent processing of material and toward designing the grinding and classification stage to produce a close approximation to this distribution as efficiently as possible. Their approaches, as summarized on the slide, include two-stage classification, dewatering by automatic pressure filters, and dry processing. Professor Laurila states that the use of two-stage as opposed to one-stage classification with recycling of the rejected portions of the classification, allows increases in the capacity of existing grinding machinery by twenty-five percent and at the same time reduces energy consumption by up to twenty percent. He points out that extensive mineral resources exist in arid countries with limited or no water supply and that additional work is needed on dry processing. The use of pneumatic classification in conjunction with two-stage classification leads to improved control of finds in improved dusting control.

Slide 11. Turning now to later stages of processing, let us consider the preparation of advanced engineering materials beginning with ceramics and going on to metals and polymers. The Division of Materials Sciences of the Department of Energy has recently

sponsored a number of workshops under the Council on Materials Science, the workshop on high temperature ceramics, for example. This Council concluded that "the major and overriding problem of high performance ceramics is that components with desired properties and microstructure cannot be reliably and reproducibly manufactured." In exploring this subject the Council focused on processing from powder rather than the melt because this is the major form of ceramic processing and focused in particular on microstructure development and control. They listed a number of areas in the physics and chemistry of particles where fundamental research is needed but drew attention especially to "what are the inter-particle forces and mechanisms that cause particle agglomeration?" and, "what are the physical-chemical characteristics of solid-fluid interfaces?" For the rheology and properties of particulate assembly they again listed a number of areas but drew special attention to "what are the particle, fluid, and interfacial factors that determine the structure and flow behavior of solid-fluid systems under various external forces?" For microstructure evolution itself they drew attention to the question "what are the effects of solid state reactions, second phases, and phase transformations on densification mechanisms and microstructure evolution?"

Slide 12. A recent analysis at the National Bureau of Standards of very promising new families of materials for which the technology is developing and an improved science base would probably result in high payoff are listed in this slide. These include two types of polymers, polymer alloys, that is blends of polymers, and biaxially oriented polymers. They include three types of processing applicable primarily to metals but in some cases with potential for ceramics as well. These are rapid solidification which can be used to produce material with at least one small dimension including powders, sheets, and surface layers, with combinations of composition and structure not obtainable by other methods. The glassy metals and the rapidly solidified powders of unusual phase composition plus the new forms of glasses obtainable by rapid quenching or molecular beam deposition techniques are promising areas here. Thixocasting and rheocasting are exciting areas with promise for the shaping of metal parts with increased processing control directly to net shape. The dual phase steels are, of course, an extremely exciting development for the transportation industry and I will come back to those a little later.

Slide 13. Let's turn now to the second issue. The National Materials Advisory Board stated that "the increasing pressure on materials research and development to show short-term results must be reduced if long-term technological and economic benefits are to be realized.

"With the increased emphasis on short-term, immediately usable results in both industry and government, long-term research necessary to supply innovative answers to present and future materials problems has been curtailed. When manufacturing companies face a profit-squeeze, research is usually one of the first activities to be reduced to improve current earnings. Any surviving research personnel are often reassigned to look either for ways to solve immediate production problems or for new products that will soon have an impact on profitability. The same situation has developed in federal funding of research; although the most recent federal budget requests show some modest increase in research monies, the trend for many years has been to reduce research funds. This pattern of diminished research by both industry and government has contributed to a reduction of innovation in materials technology in the U.S. that is a factor in the slackening of domestic productivity. Either a larger fraction of present materials research and development expendi-

tures could be supporting long-range studies, or the total national research effort could be increased to support more funding of long-range research. Such long-range research should be related to important needs and have a reasonable probability of success."

Slide 14. The question of how much research contributes to innovation and productivity and to economic growth in general is one that is much debated. Apparently it is difficult to demonstrate a simple quantitative functional relationship but five economists quoted here have concluded that "the contribution of R&D to economic growth and productivity is positive, significant, and high."

Slide 15 shows data compiled by the National Science Foundation which and was quoted by Dr. Arthur Bueche in a paper on investment and innovation. Dr. Bueche points out that R&D spending in the United States as a fraction of gross national product has been declining since 1965. A further, and very important point, is that approximately half of the R&D in this country is in support of defense. In Japan and West Germany, by contrast, the R&D budgets for defense are minimal and virtually all of their R&D funds are aimed at promoting economic development and the advancement of knowledge. Dr. Bueche goes on to paint a rather grim picture in terms of technical manpower. He states that Japan alone with less than one half the population of the U.S. may have by now as many engineers and scientists working in R&D activity as the entire United States. The U.S. effort appears not to have grown between 1970 and 1976 while in contrast Japan's efforts increased by about fifty percent.

The third critical issue shown in Slide 16 is closely related to the second. The National Materials Advisory Board stated that "mechanisms must be established to promote cooperative materials research and development among industry, government, and universities.

"At present there are adversary aspects to the government-industry relationship which discourage cooperative materials research and development. If this relationship could be improved and closer ties established with universities by both government and industry, it would appear that the U.S. materials science and technology base could be strengthened.

"American industry engages in few cost-sharing materials R&D activities with government participation. The Japanese, on the other hand, encourage close cooperation between industry and government in the development of new materials technology in, for example, electronics and steel. University participation might be made easier by greater funding for cooperative studies with industry or by tax incentives that would offset business grants to support academic research. Clearer understanding of or relaxation of anti-trust barriers to intercompany R&D might also be useful."

Slide 17. One example of rather clearly identified needs for government/industry/university cooperation is provided by the analysis carried out by Dr. Harris Burte of the Air Force Materials Laboratories. Dr. Burte found a strong need for focused fundamental research, that is, for research aimed at improving the science base in areas of perceived technological need. In particular he found a good case for the need for work in the two areas of processing science and the science underlying advanced means of nondestructive evaluation.

Slide 18. Let us turn to some international viewpoints. Dr. Umberto Colombo, Head of the Italian Atomic Energy Commission, presented a talk on "a view on strategies for international cooperation" at the International Materials Congress. Dr. Colombo contrasted the free market strategies with those of the planned economies, pointing out that both have advantages and disadvantages. In the free market case, he points out that the very virtue of the short-term responsiveness causes difficulties with anticipation

of long-term trends. In the planned economies, on the other hand, their attempt to plan for long-term trends causes them to lock in to rigid plans and carries the danger of an over-commitment to a wrong strategy. His suggestion, in essence, was that a strategy which he called technological pluralism should be followed. In essence, he suggests that cooperation between countries and long-range planning focus on the development of options, but that the decision to implement these options be decentralized as much as possible.

Slide 19. It was interesting to have at the same International Congress a view from the Socialist Bloc. Dr. George Koranyi from the Ministry of Heavy Industry in Hungary discussed cooperative projects carried out by the Council for Mutual Economic Assistance made up of six Socialist Bloc countries. He listed a number of activities in the energy and materials area and I have selected four which I think will be of interest to you. These are the mechanization and automation in open pit mines and the reclamation of the environment afterwards. The second area is completely mechanized mining techniques for mining at great depths. The third area is the development of advanced methods for coal gasification, and the fourth area is the development of new catalysts.

Slide 20. The fourth critical issue concerns the increasing energy costs for producing materials. The National Materials Advisory Board stated that "the problems associated with increasing energy costs for processing materials need to be resolved.

"The large and sudden increases in energy costs, most extreme where oil and natural gas are involved, have made the production of most materials more expensive. The increased fuel costs have affected not only the primary reduction, melting, or material synthesis costs, but also all of the energy-intensive subsequent forming or fabricating costs. In some cases alternative materials with minimum 'energy content' might have to be found for use in future designs, and the resulting changes in materials technology would probably require long lead times and new capital investment. Such substitution might render some old production capacity obsolete or underutilized with accompanying economic and social dislocations. In other cases, the proper form of energy for processing a given material may cease to be available, again bringing about disruption with sociotechnical consequences.

"Environmental costs are also linked to energy costs where fuels used in materials production require extensive pollution abatement expense to meet EPA regulations. In some cases the legislated regulations have exceeded the technology available or the cost of meeting the regulations has exceeded the capital available (as in the copper industry)."

Slide 21. Let us look at the probable future for energy costs as seen by the World Bank. Here we have the cost of petroleum from 1970 through 1977, both in current dollars, the top figure in each of two cases, and in constant dollars, the bottom line in each of the two cases. The first case is projected to 1990 on the basis of an OECD growth rate of three and one-half percent which is the low extreme considered by the Bank, and the other, an overall growth rate of 4.9 percent, which is the highest case that they consider plausible. In the low case in constant, i.e. inflation adjusted dollars, they predict the price of oil not to rise at all, although in current dollars it will more than double. In the high growth rate case, the price of oil increases about 25 percent in constant, inflation adjusted dollars, but it nearly triples in terms of current dollars. This somewhat tranquil view of the future makes one wonder if economists in examining the history of the black plague would find anything more than an example of the smooth operation of the working of laws of supply and demand. At any rate, the price rise which has already taken place, the prospects of

future price rise, and the uncertainty of supply are causing great pressures to increase the energy efficiency of materials processing.

Slide 22. Unfortunately the effort to increase energy efficiency is complicated by the simultaneous need to improve pollution control. According to Dr. Uchida of the Nippon Steel Corporation, the Japanese have put into effect an extremely progressive pollution control program. I'll show you some slides on the results in a few moments, but let us concentrate now on what it has cost them in terms of energy efficiency. They installed extensive flue gas desulfurization and dust and soot control clean-up devices. As a result it increased the energy required by 100 kwh per ton of crude steel, which is about 16 percent of the total energy required by the Japanese steel industry.

Slide 23. At the same time that their energy requirements have been going up 16 percent to control pollution, they have had a program to reduce overall energy consumption by 10 percent and they have met their goal. Dr. Uchida lists the following areas of energy saving: improved blast furnace fuel rate, increased BOF gas recovery, increase in the ratio of continuous casting processes used, improvement in reheating furnaces, increased use of continuous annealing and processing, recovery of waste heat, and improvement of rolling yield. Dr. Uchida states that the peak of expenditures on pollution control has been passed, suggesting that the Japanese steel industry is in a very strong position to continue its very successful world competition and that any hopes that the need to meet pollution requirements in Japan will reduce their competitiveness are probably doomed to disappointment.

Slide 24. The fifth critical materials issue identified by the National Materials Advisory Board concerns materials in energy systems and the way in which the Federal Government has supported work in this area. Let me emphasize that the following quotation from the National Materials Advisory Board is not necessarily my own view.

"The means by which the Federal Government supports energy-related materials projects should be defined.

"Much attention and substantial federal funding have been devoted to energy programs, including some limited investigations related to materials for energy systems and the effects of higher energy costs on materials. There is a serious need, however, for decisions regarding both the kinds of energy-related materials projects the federal government should support and the ways in which such programs should be supported. The projects range from long-range materials research for future energy systems through development of materials for demonstration plants to investigation of current materials failures in traditional fossil fuel generating plants. Federal participation has taken a variety of forms, but usually has been limited to either in-house materials studies in the DoE national laboratories, to direct grants to universities and industries, or to procurement contracts to industry. Not only do these funding mechanisms need study as to their effectiveness, but the various cost-sharing possibilities offered by the Cooperative Agreements Act of 1977 should be examined.

"The problem of suitable materials for energy generation systems is a critical one as many of the energy producing processes have serious materials limitations. This appears to be true for solutions to both near-term energy problems such as coal conversion and to long-term energy problems such as cost-effective solar electric energy."

Slide 25. In this connection it is interesting to notice that apparently some U.S. firms are now more interested in at least a limited form of cooperation with the Federal Government in energy-related materials research.

Slide 26. The sixth critical issue concerns the need to detoxify, store, and dispose of hazardous materials. The National Materials Advisory Board found that "safe and efficient means must be established to detoxify, store, and dispose of hazardous materials ranging from nuclear wastes to hazardous chemicals.

"There are great disparities in the ways in which various hazardous materials are disposed. Some of these materials are dumped in landfills, some are burned, some buried at sea, some are stored in tanks or ponds awaiting either new technology or a decision as to what disposal technique is acceptable. Part of the variation is due to lack of knowledge of the long-range effects of the materials, thus some of the differences stem from lack of agreement as to the risks involved. There also appears to be only a small body of disposal technology available to help solve the problems."

Slide 27. Turning again to the paper by Dr. Uchida of Nippon Steel Corporation, we see here results on sulfur oxide control. The upper figure shows that in 1973 they were well above the standard of 0.4 ppm SO₂ concentration. By 1977 they have gone well below the air quality standard and are now apparently in compliance. The lower part of this slide shows a measure of the emission from the steel works. The two lines on this slide indicate reduction in the content of sulfur in the fuel used and in the sintering ores. Thus, the good results on sulfur oxide control are achieved only partly by clean-up and in part by improvement in the quality of raw material. There may be a problem for the future here if these relatively clean raw materials rise in price.

Slide 28, again from Nippon Steel, shows results on dust control. Here the use of bag houses and precipitators has reduced dust emissions in 1977 to about 20 percent of their value in 1970. Again, the Japanese program seems to be very thorough and effective.

Slide 29. Turning to another and very difficult area of hazardous material disposal, we have the question of nuclear waste disposal, a very urgent question which will remain an urgent question even if commercial nuclear power did not develop in the United States. There is so much military-related nuclear waste to be disposed that this issue must be dealt with in any case. The conventional technology proposed until quite recently centered around the use of glass as a medium to contain the hazardous radioactive wastes. This is a practical technology in the sense of the ability to cast and handle a large amount of waste in practical form in glasses. However, the stability of the glass and its solubility under long-term geological conditions have come increasingly into question. Perhaps the most telling general argument against glass is the geological argument that obsidian glasses found in nature are all geologically relatively young, whereas some crystalline forms of material are very ancient indicating much greater long-term stability. Thus, in the last few years, intense activity on ceramics as a storage medium has developed. The problem is to find synthetic minerals which, on the basis of geological evidence, would be stable under geological conditions for long times which would permit the inclusion of a substantial amount of waste atoms in their structures, and which could be processed in a practical manner. Some of the leading research programs include the so-called supercaline work at Penn State University and the synthetic rock work at Australian National University.

Slide 30. The seventh critical issue concerns better assessment of environmental, safety, and health risks. The National Materials Advisory Board said "the environmental and health risks in processing and use of materials need to be better determined, better applied to regulatory decisions, and better explained to the public.

"In the last few years the public has become quite aware of and concerned about the threats to environment

and health posed by the processing and use of many materials that were long regarded as harmless. Much detailed data on hazardous materials is now being collected by more and more sensitive methods, and risk/benefit ratios are being used increasingly to provide a basis for decision-making as to which materials should be used or not used in specific circumstances. One of the classic problems that remains is how to classify materials as human carcinogens based on (1) expensive animal tests, or (2) less costly, rapid laboratory tests. The communication to the public of the results of such technical studies is complicated by the emotional response that the subject stimulates in many people."

Slide 31. Let me give one example of the difficulties associated with risk assessment. These pictures show asbestos in block form and in fiber form. Presumably the dangers to health are associated with the fibrous form and tolerable limits are therefore based upon techniques for collecting dust samples and analyzing the number of fibers per unit volume of the sample. Unfortunately, this may result in overly strict enforcement. Slide 32 shows a picture of talc which also occurs in block form and in fibrous form. The question is, are talc fibers hazardous? If not, can one distinguish in sampling between the talc fibers and the asbestos fibers? This is only one example of the thorny technical problems both in materials science and medicine to be faced in this important but very difficult area.

Slide 33. The eighth critical issue concerns conservation by better design, substitution, and recycling. The National Materials Advisory Board said "the possibilities for materials conservation by better design, substitution of less critical materials, and recycling need to be determined.

"There is a need to conserve materials more effectively by evolving engineering and design approaches so as to build products that can be: made from readily available materials, made more repairable, more readily maintained, more reliable in operation, longer lived, and more easily recycled. Adequate attention should also be given to consideration of the tremendous materials savings that might be possible through reduction of wear and corrosion. (It is estimated that corrosion alone costs the U.S. \$70 billion per year.) The need for the conservation of certain critical and strategic materials also requires that a better approach to substitutability be developed; at the present time no general methodology for anticipating substitution exists, so each situation that arises is treated in a specific, ad hoc manner."

Slide 34. An interesting example of substitution as practiced by a foreign country is provided by Mexico. Mexican aluminum use is 90,000 tons per year of which 50,000 tons are produced within Mexico from imported bauxite and 40,000 tons are imported. At the same time, Mexico produces 270,000 tons of zinc per year of which it uses 70,000 tons, and exports 200,000 tons at a relatively low price. They would like to reduce their importation of aluminum and increase their value added in the case of zinc so they have developed a special series of alloys in which they use large amounts of zinc. Thus, they are able to reduce their aluminum content and aluminum-zinc alloys to the range of 17 to 40 weight percent, apparently with acceptable properties for many applications. This is not an alloy which is likely to find widespread use in all countries, but for Mexico's particular situation it seems an ingenious development.

Slide 35. Another example of substitution is indicated by an analysis presented by Dr. Becker of the Mobay Corporation. He compares a fender liner made out of three materials, either steel, aluminum, or plastic. He presents an analysis of the energy required in units of equivalent gallons of gasoline to manufacture the item and the energy consumed in five-year operation on an automobile. The sum of these two figures gives the

total energy. For steel, we see that it requires 3 gallons of gasoline to make the 15-pound part and 11 gallons to operate, giving a total of 14 gallons gasoline equivalent. For aluminum, the 5-pound part requires 6 gallons of gasoline equivalent and consumes 4 gallons in operation, leading to 10 gallons total. For plastic, the part would weigh slightly more, 6 pounds, would require 2 gallons gas equivalent to manufacture, and would consume 5 gallons over the five-year operation. On this basis the total for plastic would make it preferable on an energy basis alone. However, the competition is more complicated than indicated here. One aspect of this further complication is indicated in the next slide.

Slide 36. Here we see a plot of tensile strength vs. formability for various steels. This illustrates the exciting promise of the so-called dual phased steels which allow a combination of high strength with high formability. Substitution of such steels might significantly alter the comparison shown on the previous slide.

Slide 37. Turning now to recycling, it is interesting to look at a foreign situation. Elaine Morin of the French Scientific Mission states that the French goals are to reduce copper imports by 50 K tons or approximately 15 percent. It is interesting to notice that they currently recycle only 35 percent of their copper in contrast to the United States where we recycle about 61 percent. For paper they want to increase recycling from 1.8 million tons to 2.3 million tons. In glass they are hoping for a more than five-fold increase in recycling, and in polyvinylchloride for an increase of 100-fold. To encourage this the French government has provided assistance in funding some pilot plants and is supporting research in areas such as the reuse of copper with impurities.

Slide 38. The ninth critical issue concerns predictive capacity. The National Materials Advisory Board stated "A sound predictive capability must be provided to warn of impending or possible changes in materials supply and demand on both a national and global basis.

"Materials shortages can develop rather suddenly if the analysis of materials supply and demand is not carried out with adequate data and by probing, thoughtful techniques. Such predictive systems require not only complete and detailed information from both government and industry, but also a means of quickly communicating the results of the analysis with a consistent record of accuracy to be credible and effective. It is particularly important that such systems be responsive to the effects of alternative government policies that may affect supply or demand."

Slide 39. The Materials Economics Workshop at the International Materials Congress considered the supply and price of materials and came to the conclusion that there was no prospect of a near-term run-out due to any fundamental shortage of materials. They foresee instead instabilities in supply and crises because of long lead times and large investments required to open up and bring into production new sources of supply.

Slide 40. In conjunction with this workshop, Mr. Singh of the World Bank made a prediction of the price of selected metals and minerals in inflation-adjusted 1977 dollars. Dr. Singh's predictions are for the long-term and do not include short-term fluctuations. Bearing this in mind it is interesting to note that for copper he foresees a price in 1990 in constant dollars about midway between the present price and the relatively high price of 1970. For iron ore, again he sees an intermediate price; that is, he is not forecasting for these two commodities that the relatively high prices of the 1970 period will return by 1990. For tin he forecasts a drop to a price level intermediate between the present price and the lower 1970 price. For nickel he foresees a recovery almost to the levels of

1970, and for bauxite alone among the commodities listed here, he sees the 1990 prices being somewhat higher than both the 1970 and the 1978 prices. For the general index of metals and minerals he foresees an increase from current level of 90 to a level of 126 which is still considerably less than that in 1970. The view from the World Bank seems to be then, no prospect of run-out, average prices rising in real terms but not to the levels 1970, with a warning that superimposed on this may be large short-term fluctuations in supply and price.

Slide 41. The tenth and final critical issue concerns actions that could be taken to reduce the consequences of these short-term but possibly very punishing fluctuations in supply and demand. The National Materials Advisory Board said that "if the U.S. must depend to a greater extent on its own materials resources, the effects on industrial activity should be considered, as well as steps that might be taken to ameliorate the possible consequences.

"If materials supply to the United States becomes increasingly curtailed, the alternatives to imports must be carefully considered. These would include not only more intense contingency planning for conservation, substitution, and recycling of strategic materials, but also the development of low-grade ore deposits that may not be economically attractive at present. The rationale for a national strategic and critical materials stockpile should be thoughtfully explored and its real costs and benefits examined closely as well as those of the alternatives."

In commentary, it may be said that any of these options involve substantial investments which will have value only in the case of contingencies which may or may not occur. The issue of stockpiling, for example, has been economically modeled and the attempt to calculate an economic best strategy requires data on supply and demand elasticities plus probabilities of occurrence for emergency situations which are guesses at best. The problems with this issue appear to be more political than technical and I do not propose to discuss them any further.

This rapid survey of the ten critical issues in materials as seen by the National Materials Advisory Board certainly does not do justice to the many materials programs which I listed at the beginning of this talk. I hope, though, it has given a useful perspective and that some of the illustrations have been interesting.

Thank you very much.

SCIENCE IN THE YEAR 2000

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Research planning for the Year 2000, as suggested in the title, sounds like a contradiction in terms. On one hand it is not unreasonable to expect current basic research efforts to have yielded exciting technologies by the Year 2000. On the other hand, it is quite improbable that any examination of today's basic research scene would permit us to foretell the areas of greatest revolutionary change which will occur 20 years hence. The dilemma of scientific prediction, or that of the planned breakthrough, has been likened to the problem of the surfer trying to select from a sea of ripples the most promising potential wave upon which to mount.

Those who doubt the difficulty of this problem need only examine in retrospect the predictive power of an observer 20 years ago. At that time we did not know of integrated circuits and could not anticipate the great potential of this technology, our imagination being limited by discrete components and ceramic vacuum tubes. Much of modern electrooptics had yet to be born and the biological revolution had not yet begun. We were living in an era of energy plenty and environmental abandon. What we find commonplace today was thus quite beyond the predictive ability of the observer of 1959. Fortunately, however, in spite of their inability to predict the future in detail, research managers of the 40's and 50's are responsible for having laid the foundation for all of the rapid advances in computational and optical technology which burst open in the 60's, their inability to make detailed predictions notwithstanding.

The problem of planning a research investment strategy has much in common with that of managing a diversified portfolio of investments. In both cases the power of hindsight greatly exceeds that of foresight. And, rejecting serendipity, in both cases we search for fundamentals to guide us in long term investment planning.

In the area of national defense, difficulties are compounded by the need to account for rapid changes in international affairs. Along with, and perhaps driven by, technology the world's political scene has changed considerably during the last 20 years and may be assumed to continue to follow quite unpredictable political paths. Meanwhile, resources for research have diminished, resulting in even greater demand for rational means of identifying areas deserving of expanded resource investments while, more painfully, also selecting areas in which resource contraction can be afforded.

This talk describes a method of structured thinking designed to guide resource allocation for areas of basic research spanning life sciences, physical sciences, and information and mathematical sciences. The method assumes that although we perceive rapid change in the world, this perception is driven by transitory parameters and that beneath it all there exists very fundamental factors which change in fairly predictable and inexorable ways. It is upon this fundamental set that we focus our attention. The fundamental factors include, for example, the demography of population groups, the existence of population groups in specific land areas, the food, climate and natural resources distribution in the world, and travel routes which connect populations with land areas and natural resources, etc. Through an analysis of the geo-political impact of these fundamental factors, several key planning postulates for basic research were derived. Five of these postulates were addressed to some extent in this talk. The five postulates are: (a) that the United States will continue to find itself in a numerically adverse situation in terms of both military force and population with respect to potential opponents; (b) the denial of energy and material resources will become a common feature of international relations; (c) economic conflict beyond that normally associated with international trade could become commonplace; (d) space systems will continue as a military asset of growing importance; (e) computational devices and systems, as well as the science of computation and artificial intelligence will expand opportunities and capabilities for those nations in leading positions to utilize this power.

The final step in this planning process requires that the five postulates be projected into terms which relate to the Air Force mission. This projection results in the identification of a number of fields of basic research in which creative science should be stimulated and supported in anticipation of future changes in required Air Force capabilities. This strategy of supporting basic research in broadly defined, but carefully selected, areas chosen on the basis of fairly predictable geo-political fundamentals, is the strategy which appears to be the best able to develop a scientific and technological posture capable of responding to the unpredictable unfolding of political events.

CORROSION, THE SILENT SCOURGE

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ABSTRACT

Corrosion causes the users of durable goods to incur costs for their maintenance and replacement. When best practice corrosion-control technology is used, these costs are unavoidable, and with constant economic factors such as discount rates and tax structures, can only be reduced by technological development. When best practice technology is used, a portion of these costs is avoidable. An estimate of these costs for all sectors of the U.S. economy will be presented. Data will be given for the producing sectors as well as for final demand. The costs will be given for corrosion maintenance and control, for equipment replacement when such replacement is because of corrosion, and for redundant capital equipment when such redundancy is required because of corrosion.

In early 1976, the U.S. Senate, in its report on the appropriation bill for the National Bureau of Standards, directed that institution to embark upon a study of the economic effects of corrosion. The corrosion group at the National Bureau of Standards (NBS) is a technical group that had not previously conducted any formal economic studies. Hence a contract for the study was let to the Battelle Columbus Laboratories (BCL) which has both economic and corrosion expertise. The staff of BCL and NBS worked very closely together in defining the scope of the work and in the collection of data. In the fall of 1977, BCL delivered its report(1) to NBS. From this report, NBS prepared its own report for the Congress(2) and in the process extensively revised some of the figures in the BCL report. This paper is a summary of the results in the NBS report.

Corrosion, defined for the purposes of this study as the degradative interaction of a metal with its environment, is only one of a number of degradative processes such as wear, fatigue, fracture, ultra violet degradation, etc., that affect materials. Corrosion, however, is unique in that a significant number of studies of the costs associated with it have been carried out.(3-14). These are listed in Table 1. The most thorough and important of these studies is that listed under U.K. (6,7), the famous "Hoar Report." This study came to the conclusion that the total cost of corrosion in the U.K. for 1970 amounted to 3.0% of the Gross National Product (GNP), and that 23% of the total cost (or 0.69% of the GNP) could be saved by use of presently available corrosion knowledge. In the terminology of the NBS report these latter costs are "avoidable". Where it is possible to make such an estimate, it will be seen that the total costs amount to 2-3% of the GNP, with approximately 20% of this avoidable. As will be seen below, these results are completely consistent with those obtained in the NBS-BCL study,

when account is taken of the more thorough treatment by NBS-BCL, particularly with respect to the final demand sectors of the economy, -Personal Consumption, Government, and Private Fixed Capital.

DEFINITIONS AND METHODOLOGY

DEFINITIONS - In order to carry out the directives of the Congress it was first necessary to define the "economic effects." The definition of these effects is very closely related to the costs of corrosion. The economic effects were taken to be

"Those resources (materials, energy, labor, capital) which, in the absence of corrosion, would be available for alternative uses."

This means simply that in the absence of corrosion, resources of materials, energy, labor and capital that are now used because corrosion exists would become available for other uses. The yearly cost of these resources thus becomes the total cost of corrosion. This definition of the total cost of corrosion, implies that the baseline for the accounting is a hypothetical corrosion free world.

In addition, however, we need to take into account that some of these costs are avoidable in the sense of the Hoar Study. Hence we also define the avoidable costs (or effects) as

"Those resources (materials, energy, labor, capital) that would be available for alternative uses if economic best practice were used everywhere."

Economic best practice means a minimum life-cycle cost. It therefore balances first-cost against lifetime and total maintenance costs and does not mean the use of the most corrosion resistant material. Indeed, in some cases, it may be economically better to use a more corrosion-prone material than a more resistant one, if the first cost is sufficiently lower. Notice that the baseline for this accounting is a hypothetical best practice world, in which everyone uses economic best practice. This implies what is certainly known to be true, namely that not everyone in the real world uses economic best practice.

The difference between the total costs and the avoidable costs gives what are called the presently unavoidable costs. The significance of these definitions is that avoidable costs can be reduced by the application of presently existing corrosion control technology, and hence their reduction involves technology transfer, while the presently unavoidable cost cannot be reduced with presently available corrosion control technology and hence their reduction requires research and development.

ELEMENTS OF THE COSTS OF CORROSION - The principal elements of the costs of corrosion are given in Table 2. These elements apply to both the total and avoidable costs. They are broken into four categories:

Capital Costs, which apply to consumer items as well as industrial and commercial equipment, include costs associated with shortened lifetime, any excess capacity that may be required because of corrosion, and the costs of any redundant equipment that may be necessary because of corrosion.

Control Costs, includes costs of maintenance and repair and costs of corrosion control (cathodic protection, water treatment, etc.)

Design Costs, includes the costs of special materials (stainless steel, copper alloys, etc.) when used because of corrosion, costs of extra materials used (heavier sections on beams, etc.) and special processing.

Associated Costs, includes such items as loss of product, research and development, insurance, and the cost of maintaining the inventory of parts and equipment needed for corrosion control. It does not include the

cost of the items in the inventory since this is accounted for under control and repair costs.

METHODOLOGY - The methodology used for the study was input-output analysis, in which BCL has extensive expertise. For this purpose the economy is divided into 130 producing and service sectors, plus final demand. Producer Capital, which is normally considered a part of final demand, was handled somewhat differently in this study, in that producer capital was considered to be an input into production(1). The economy was modeled as a steady state economy. The year chosen was 1975 at hypothetical full employment. The study was not a "scenario" study. That is, no attempt was made to redistribute the costs; they were simply collected. It was thus a comparison of three static cases: 1975 at full employment; what 1975 would have been in the absence of corrosion, and what 1975 would have been with full best-practice use by everyone.

The results will be presented as follows:

Final Demand Sectors - These are Personal Consumption Expenditures (PCE), Federal Government Expenditures (FGE), and State and Local Government Expenditures (SLGE). The costs for these sectors will be presented by the item of equipment and buildings for which the costs are incurred, e.g., automobiles. The elements included in these costs are primarily capital costs and control costs and some parts of associated costs where applicable. Design costs do not apply to final demand directly. They are borne in manufacture and are included in the next item.

Intermediate Output (I/O) - These are the costs incurred as inputs by the producing and service sectors of the economy. They include primarily design costs and control costs, with associated costs being a small portion. They are presented by the sector bearing the cost.

Private Fixed Capital Formation (PFCF) - These are the capital costs borne by the producing and service sectors of the economy. As previously noted capital costs are those occurring because of shortened lifetime, excess capacity, and redundant capital. These costs are presented by the sector producing the capital.

RESULTS

OVERALL RESULTS - The total costs and the avoidable costs for all sectors are given in Table 3. Columns are given for the BCL results and for the NBS results derived from them as described in reference(2). An estimated range of uncertainty is also given.

The total costs are \$69.7B, with a range of \$52.7-86.2B. This amounts to 4.2% of the GNP, which is in good agreement with the studies listed in Table 1, when account is taken of the more thorough coverage of the BCL-NBS study. The largest costs are in Intermediate Output and in Private Fixed Capital Formation. The primary difference between the NBS results and the BCL results arises from the treatment of the life time of automobiles and other capital equipment by BCL. Reference(2) should be consulted for details.

In the avoidable costs, a significant change was made by NBS from the BCL figures, primarily because of the lifetime assessment for various items of capital equipment, notably the automobile(2). In addition, an unknown factor labelled Y is included in the NBS results. This arises because BCL estimated that best practice could be achieved without any change in input to the manufacturing sectors as compared to the present situation. That is, there would be no changes in usage of stainless steel, copper, coatings, etc., and implies that first cost would not change. This view is not subscribed to by NBS, and the factor Y is listed to account for this. This factor is presently unknown, but is roughly estimated to be about \$6B. With this value of Y, the avoidable costs are \$10B, with the wide range of \$2-40B. This value of Y makes the Intermediate Output

avoidable costs negative, which merely means that the first cost of equipment would increase, although the net savings to the economy with best practice would be \$10B. The avoidable costs are about 0.6% of the GNP which is also in good agreement with the studies listed in Table 1.

The uncertainty in the results arises primarily from the uncertainties in estimating reliably the lifetime of equipment. These lifetimes are not well known even in the present world, and in addition estimates need to be made in both the corrosion-free and best-practice cases. This inevitably leads to a wide range of uncertainty. References(1) and (2) should be consulted for details.

SPECIFIC SECTOR RESULTS - The results for specific sectors are given in the NBS report(2) and in more detail in the tables appended to the BCL report(1). In any study of this kind, individual sectors have more uncertainty than the over-all figures, since in the over-all figures, errors will tend to cancel. In this section, representative figures will be given for each of the sectors studied.

Personal Consumption Expenditures - The most significant of the total costs for personal consumption expenditures are given in Table 4 and the avoidable costs in Table 5. The largest item is in automobiles, which appears in two places in these tables. The entry under "automobiles" reflects effects of corrosion on the life time of automobiles, which is on the average 9.6 years, and estimated to increase to 13.6 years in the absence of corrosion(1,2). However, the distribution around this average can cause serious uncertainty(2). The entry under "Automobile Repair and Service" represents expenses for repair and service caused by corrosion. All other entries contain both capital-associated costs as well as Maintenance and Repair, except for Miscellaneous Chemical Products, Maintenance and Repair Construction, and Personal Repair Service, which are solely for maintenance and repair.

Government Expenditures - The most significant of the total costs for the Federal Government are given in Table 6, and the avoidable costs are given in Table 7. The very large bulk of these costs are borne by the Department of Defense which has custody of by far the largest amount of equipment. The largest single cost is for aircraft, which is estimated to be the single largest item of capital equipment in the Federal Government. This cost arises because of redundant equipment, with the following reasoning. Approximately 30% of the time, aircraft are not deployed since they are undergoing maintenance, transfer, etc. It is estimated that 20% of this time is caused by corrosion, and hence 6% of the time aircraft are not available for corrosion-related reasons. Therefore, to maintain a certain striking force, 6% more aircraft are required than would be necessary in the absence of corrosion. The yearly costs associated with the procurement of these aircraft form the bulk of these costs. The other large cost is Government Industry. This includes the activity of civilian employees, part of whose duties is the maintenance and repair associated by corrosion in aircraft, ships, etc. For further details reference(1) and (2) should be consulted. In general, the Federal Government has good corrosion control.

State and Local Governments are not presented in a separate table. The total costs from Table 3 are \$2.4B, and the avoidable costs are estimated to be \$0.9B. The largest single item is in Building and Repair Construction which is almost totally for highways.

Intermediate Output - Representative total and avoidable costs for Intermediate Output are given in Table 8. As previously noted, these costs represent added inputs (special metals, corrosion allowance, special coatings, etc.) required by the manufacturing sectors because of corrosion, and corrosion maintenance and repair of the equipment and buildings in the pro-

ducing and service sectors. A small amount also goes for insurance and other associated costs.

This sector was the most thoroughly studied and the total costs are the best known, as is evidenced by the small uncertainty of $\pm 3\%$. In many knowledgeable industries sophisticated in corrosion control, such as Petroleum Refining and Electric Power, very good data are available.

With respect to the avoidable cost, however, the situation is quite different. As previously noted above under Overall Costs, the avoidable costs include only maintenance and repair, and the figures shown in this table and in Ref. (2) are the BCL estimate of how much could be saved by the producing and service sector by better maintenance and repair. Since the total costs include all inputs and the avoidable costs include only maintenance and repair, this accounts for the low value of avoidable costs. Moreover, in the capital equipment producing sectors (Fabricated Structural Metal, General Industrial Machinery, etc.), the achievement of best practice may actually increase the total cost, hence leading to a negative avoidable cost for these sectors. This leads to the factor Y in Table 2. No attempt was made to redistribute this factor to the relevant industries, and hence even for these industries in Table 8 the avoidable costs include only maintenance and repair.

Private Fixed Capital - Finally, Table 9 gives the most significant total and avoidable costs borne by the producing sectors for capital costs. These costs are caused primarily by the effects of corrosion in reducing lifetime of capital items, but a small part is caused by redundant equipment. The listing is by the sector that produces the capital. A listing by the sectors using the equipment can be obtained from the "Industry Indicators" discussed in Ref. (2). The rather large uncertainty indicated for these costs is caused by uncertainties in the life time of equipment as previously discussed in Section 3.1.

SUMMARY AND CONCLUSIONS

It is estimated that the total costs of corrosion, and hence its economic effects, are 4.2% of the GNP, with a range of 3.2% to 5.2%. The avoidable costs are estimated to be about \$10B, or 0.6% of the GNP with a very broad range of 0.2% to 2.4%. The range of both these estimates could be reduced by further study. By comparison of these results with previous studies, and because in such studies the errors will tend to cancel, it is believed that these results are representative of the total costs of corrosion in the economy. It is also believed the total methodology developed is better than has been used in any previous study. First, it provides a framework for determining costs, and second it provides a sound and proven economic model for determining their economic effects. As more and better data become available, they can readily be added to the present data to make the estimate of costs more precise. However, two deficiencies still exist in the study.

First, the question of added inputs required for best practice needs to be determined in detail and the results distributed to the various final demand sectors to get a net cost for those sectors. This can be done with further study.

Second is the problem associated with life time of equipment. We do not, unfortunately, know the actual range of life time of products in the economy, even in the present world. A determination of these life times would be useful not only for improving the accuracy of the present study, but many other studies, such as, e.g., materials conservation, total availability of scrap, and the effects of other degradative processes, such as wear and fracture.

Despite these qualifications, it is believed that the Congress has been given a good overall picture of the economic effects of corrosion. The results in individual sectors can unquestionably be improved, but it is believed that the overall results will prove to be correct--certainly within the error limits stipulated.

TABLE 1
Cost of Corrosion, Various Nations

Nation	Year	Cost	Avoidable	% GNP
USSR	1969	6 B Rubles \$6.7 B		
West Germany	1969	19 B DM \$6 B	4.4 DM \$.15 B	3 (0.75)
Finland	1965	150-200 M Markaa \$47-62 M	-- --	-- --
UK	1969-70	£1.365 B \$3.2 B	£0.31 B \$0.74 B	3 (0.69)
Sweden	1964	0.3-0.4 B Crown \$58-77 M	25%	
India	1961	1.54 B Rupee \$320 M		
Australia	1973	\$470 M \$550 M	--	1.5(3)
USA	1947	\$5.5 B	--	2.3
	1965	\$15 B	--	2.2
	1975	\$9.7 B	--	--
Japan	1977	2500 B Yen \$9.2 B	--	(1.8)

Table 2
Some Elements of the Costs of Corrosion

Capital Costs	
-	Replacement of equipment and buildings
-	Excess capacity
-	Redundant equipment
Control Costs	
-	Maintenance and repair
-	Corrosion control
Design Costs	
-	Materials of construction
-	Corrosion allowance
-	Special processing
Associated Costs	
-	Loss of product
-	Technical support
-	Insurance
-	Parts and equipment inventory

Table 3

Summary of Results

Sector	Total Costs (\$B)			NBS Range	Avoidable Costs (\$B)			NBS Range
	BCL	BCL Range	NBS		BCL	BCL Range	NBS	
PCE	22.8	--	15.8	10.3-21.3	15.9	--	4.9	3.8-15.9
FGE	8.1	--	7.9	6.2- 9.6	1.7	--	1.7	0.8- 2.5
S/LGE	2.9	--	2.4	1.2- 3.6	0.9	--	0.9	0.5- 1.4
IO	24.5	--	24.5	23.5-25.0	2.0	--	2.0-Y	- Y- 2.0
PFCF	24.1	--	19.1	11.5-26.7	12.5	--	6.2	3.0-19.1
Total	82.4	--	69.7	52.7-86.2	33.0	--	(15.7-Y)*	(8.1-Y)-40.9

*The value of Y is a matter of speculation, but assuming it costs between 10 and 70 percent of the expected final demand gain for best practice (extra coatings, etc.), Y would be between \$1.4 and \$9.6 B, and the total avoidable costs would be between \$6.1 and \$14.3 B, or about 10 and 20 percent of the total cost. Note that these values of Y could make the avoidable 10 contribution negative. This would mean an increased cost to manufacturers in a best practice world, to achieve a net savings to manufacturers plus final demand (life-cycle costs).

Table 4

Total Costs - Personal Consumption
Millions of Dollars

Misc. Chem. Products	159
Automobiles	8800
Trucks, Buses, Etc.	2090
Ships & Boats	143
Household Appliances	848
Radio, TV, Comm. Equip.	662
Maint. & Repair Const.	992
Personal & Repair Serv.	331
Auto Repair & Service	2075

Table 7

Avoidable Costs - Federal Government
Millions of Dollars

Gen. Ind. Mach.	74
Automobiles	77
Trucks, Buses, Etc.	77
Aircraft	557
Ships & Boats	408
Sci. Instr.	53
Maint. & Repair Const.	75
Gov't. Industry	224

Table 8

Intermediate Output Costs
Millions of Dollars

Table 5

Avoidable Costs - Personal Consumption
Millions of Dollars

Automobiles	2800
Truck, Buses, Etc.	500
Ships & Boats	83
Household Appliances	344
Maint. & Repair, Const.	347
Personal Repair Serv.	115
Auto Repair Serv.	726

	Total	Avoidable
Fabricated Structural Metal	1046	6
Screw Machin Prod. & Stamp.	681	2
Misc. Fabricated Metal Products	589	3
General Industrial Machinery & Equipment	668	20
Special Industrial Machinery	532	1
Furniture and Fixtures	608	3
Petroleum Refining	882	30
Steel	728	15
Automobile	1350	22
Electric Power	2690	56
New Construction-Public Utilities	1485	32
Wholesale and Retail Trade	606	272
Finance, Etc.	617	280

Table 6

Total Costs - Federal Government
Millions of Dollars

Metals	262
Gen. Ind. Mach.	144
Automobiles	208
Trucks, Buses, Etc.	309
Aircraft	2460
Ships & Boats	905
Comm. Equip.	1033
Sci. Instr.	103
Ordnance	224
Maint. & Repair Const.	375
Gov't. Industry	1494

Table 9

Private Fixed Capital
Millions of Dollars

	Total	Avoidable
Fabricated Structural Metal	1044	548
General Hardward	282	106
Engines and Turbines	334	67
General Machinery	851	447
Farm Machinery	1221	224
Construction Machinery	1415	283
Automobiles	3640	1370
Trucks, Buses	2006	401
Aircraft	227	45
Railroad Equipment	267	140
Industrial Controls	340	68
Service Machinery	568	213

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DEFINING NEW DIRECTIONS FOR CORROSION RESEARCH AND DEVELOPMENT

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ABSTRACT

In recent years maintenance costs have generally exceeded acquisition costs in the life cycle of aerospace systems. As usable system lifetime has increased, corrosion problems have become a major factor which presents a new fundamental challenge to the research community. Through a series of AFOSR/AFML corrosion workshops, a number of new and promising directions for corrosion research were identified, and approaches for current development where outlets for current research exist were specified. A four-column tabular format listing General Problems/Needs, Windows, Reduction to Practice/Development Possibilities, and Focused Research Needs was found to be particularly useful. "Windows" are specific applications where the R&D can be immediately applied. The keying on windows to indicate research directions and focus discussion has been utilized successfully at several subsequent scientific meetings. While the original study was done specifically for the Air Force, the approach could be used for any large organization. Examples of current R&D needs and possibilities are given.

Despite significant economic incentives (1), and a growing national attitude that it is also morally proper to conserve finite resources and avoid waste, corrosion R&D is not a rapidly expanding field (2). It has begun to receive increased attention, but many of those who might use its results are often disenchanted with its past performance or future potential. Those who are attacking its problems from a fundamental point of view still seem to be relatively "few and far between."

Two years ago Frank Kelley and one of us at the Air Force Materials Laboratory undertook an analysis of the health of the materials-science base in the United States from the viewpoint of the needs of the aerospace industry. Among the stimuli for this was the recognition that as a result of obvious requirements to reduce cost and increase reliability, many sources of R&D support were providing large resources for relatively short-range, "put it into use" developments. There was concern as to whether this was an inverted pyramid resting on an inadequate base of fundamental knowledge. It should be clearly understood that this was an analysis from the viewpoint of need; it did not address that portion of the science base (often referred to as truly basic) which is knowledge driven and motivated by the extent of new understanding which can be obtained irrespective of the predictability of its utility. The latter portion of the science base should be judged on the quality of the investigators and research, not its relevance to definable need; and we do not imply that need-related work should be supported at the expense of such truly basic work. The most affluent society in history should support a very significant, truly basic activity. It will enrich our culture and inevitably

satisfy our needs in innumerable ways. It is, however, appropriate that some portion of fundamental-research activity in the country be motivated by perceived needs, and the purpose of our analysis was to determine whether there were major gaps in such need-related national activity. The current "National Symposium on Wear and Corrosion" is also obviously concerned with need-driven science, and a review of the Burte-Kelley study and its findings is appropriate.

The process used was to prepare two straw men, one identifying long-range generic needs and concerns for aerospace-materials technology and the other listing specific needs for fundamental knowledge in several broad areas or disciplines. The former was derived from planning studies and personal knowledge; the latter was generated during a budget-allocation exercise being conducted to define the laboratory program for a future fiscal year. For example, if proposed new development programs were rejected by the laboratory senior management because there was no adequate knowledge base to support the proposals even if the goals were desirable, a need for knowledge could be identified. Ongoing or successfully advocated new development or application programs were reviewed to identify instances where it was felt that the availability of additional knowledge would increase the probability of success or make the results more generally useful. Proposals directly from the working level to obtain more fundamental knowledge to point the way for future developments were obvious additions to the growing list of specific needs.

All the items identified were sorted into a set of disciplines or multidisciplines. For each item the following question was posed: "Is there a minimum level of activity consisting of two to five fundamental research groups (depending upon our judgment of the importance and difficulty of the item) doing productive work in the general topic of the item which might yield knowledge which could be incorporated into development programs or engineering use in five to ten years?" Note that this decoupled from the specific need for knowledge which generated the item. If there were not a minimum number of two to five such groups (each consisting of at least one active professor and several graduate students), the topic was identified as being a gap and left on the lists.

The straw-men lists thus generated were then iterated through more than 50 industrial and university groups throughout the country. The industry people were usually asked to focus on the areas where they could identify a need for new fundamental knowledge, i.e., what was left off the lists. The university people were usually asked to focus on the assessment of whether minimum productive activity was underway in a specific topic. Both were asked to comment on the long-range generic needs and concerns. The

early proposals were expected to generate controversy and additional input. This indeed occurred, and such input was incorporated into successive versions of the long-range needs and lists of specific gaps. As the rate of change decreased, tentative conclusions were drawn and exposed to the iterative process, which now included people who had been instrumental in earlier reviews of materials science and technology such as the COSMAT study, other government agencies, and selected gatherings of knowledgeable individuals such as the Materials Advisory Board and a meeting of representatives to the Federation of Materials Societies.

Table I shows the major long-range generic needs and concerns at a late stage in the process, after which there was almost no disagreement with the statements shown. Note that the first two items are technical needs; the last three are institutional concerns. Eventually in the iterative process there was little further change in the relative sizes of the lists of gaps under the nine disciplines or multidisciplines eventually chosen as a "table of contents" of the materials-science base. (These disciplines/multidisciplines shown in Table II changed during the iterations until most participants indicated comfort with and acceptability of the set shown.) The final conclusions, based upon the relative lengths of the lists of gaps and consistency with long-range needs, are shown in Table II. Note that "Surface Physics and Chemistry" was an area of broad need with many significant gaps, despite the fact that much good surface physics and chemistry is underway at American Universities. (It should be re-emphasized here that the purpose of the study was to identify areas of gross inadequacy. This does not imply that even more effort in solid state physics would be undesirable, rather that the potential of this discipline is well recognized and that there are very few topics in it where at least minimum effort is lacking.)

Table I - Long-Range Generic Needs And Concerns of Aerospace Materials Technology

Few new systems will be introduced in the future; current systems must last longer

- high acquisition costs, maintenance costs

Air Force continues to require materials which are used near their limits where failure can be disastrous

Changing nature of industrial research shifts major burden for high-risk, innovative research to federally funded programs

Industry/university interface is weak

Effectively coupled, multidisciplinary programs at universities are rare due to institutional barriers

Although the analysis was initiated to evaluate the health of the materials-science base from the viewpoint of the Air Force in particular and the aerospace industry in general, it became apparent during some initial visits to materials producers and fabricators serving several sectors of the economy that the results might be similar for all sectors. The long-range needs and generic concerns shown in Table I are as applicable to the needs of new energy generation or conversion technology, for example, as they are to aerospace. Therefore, during the later iterations, individuals and companies representing many

Table II - Applicability To Aerospace Needs Of The 1977 Materials-Science Base

<u>Inadequate</u>	<u>Marginal</u>	<u>Adequate</u>
Processing Science	Metallurgy Ceramic Science Polymer Science	
Surface Physics and Chemistry	Mechanics Thermophysics and Chemistry	Solid State Physics
NDE Science		

different potential uses of materials science and technology were involved. It is believed that the conclusions indicated in Table II need not be restricted to aerospace and are generally applicable.

The long list of gaps under "Surface Physics and Chemistry" was in large measure due to a general perception that relatively little of the work underway was really relevant to complex degradative processes such as corrosion and wear. This was not surprising to many of those who participated in the survey since the problems involved can be very difficult. It is a risky area for a young professor on tenure track. For older, well-established people there often seems to be a feeling that such "complex" subjects are somehow inelegant and to be avoided. Sources of support for fundamental research often seem to share this feeling. A major concern was the generic problem in materials technology of life prediction and accelerated testing (Table III). Many environmental factors, material conditions, and design/configuration specifics interact in very complex ways to produce the observed result.

Table III - A Generic Problem - Life Prediction And Accelerated Testing

- Need for failure models
- Complex and multidisciplinary
 - Elastometric seals and sealants
 - Corrosion
 - Lubrication
 - High-temperature coatings
 - Creep-fatigue-environment interaction
 - Superalloys
 - Advanced composites
 - Ablators

Even applied corrosion R&D is not at present an adequate national activity. Very short range problem-solving activity is rarely expanded to provide understanding of application beyond the immediate situation. Only moderate resources are available for exploring the reduction-to-practice possibilities inherent in existing knowledge which might provide generic new capabilities. The authors have often had difficulty defending existing--much less expanded--budgets for work of this nature, despite the experience that in recent years maintenance costs have approached or even exceeded acquisition costs in the life cycle of aerospace systems. Granted that a better application of existing technology in initial design and production could yield more maintainable hardware than in the past (3), many areas must still exist where usefully improved materials, protective

processes, inspection or life prediction methods, etc., could be developed. In addition, there is the increasingly important problem of how to manage large existing fleets of aircraft. For these it is too late to incorporate a better balance between acquisition cost and maintenance cost into the initial design. Certainly, new technology arising from new knowledge should help reduce the maintenance costs. Yet there have been too few good suggestions from academic research institutes or industry which effectively combine significant technical possibilities with a clear recognition of realistic needs to propose attractive applied R&D programs.

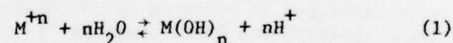
Recognizing these deficiencies in both need-driven fundamental research and development-oriented activity, the authors have initiated (4) or participated in several workshops or other forums in the last few years to encourage a better identification of both needs and possibilities for such corrosion R&D. The approach used was to stimulate both the horizontal (mechanics, chemistry, metallurgy, etc.) and vertical (research, production, test, maintenance, engineering) interdisciplinary coupling which was felt to be necessary.* The goal was increased enthusiasm for working in, as well as support for, corrosion R&D. The insights gained from these experiences and some illustrations of both the problems and the potential will now be presented.

The workshops attempted to bring together fundamental-research scientists working in the various disciplines which might be appropriate, acquisition and logistics engineers, and field-level maintenance personnel. Management and resource-allocation people from both government and industry were often included. It was hoped that the "scientists" would describe the reduction-to-practice possibilities emerging from current research in a sufficiently evocative way to capture the interest and stimulate the imagination of the engineering and user people. Similarly, it was hoped that the user community would describe their needs in sufficient detail to do the same for the scientists. Ideally, there would be a synergistic effect to help define both new development possibilities and specific areas where fundamental research might be fruitful. Although these were significant successes, there was also considerable difficulty.

Many--if not most--of the individuals who were expected to provide scientific possibility input were hesitant to "open up" or really try to stimulate the interest of the user people. Suggestions of novel approaches frequently caused inhibiting criticism. For example, the need for systematic studies of the role of hydrogen in metals often arose. The advent of new analytical tools with improved precision and sensitivity for hydrogen determination has been helpful (6). Progress in the 1960's in processing out hydrogen from high-strength steels and the development of alloys such as 300M with increased tolerance to hydrogen has also done much to eliminate the service failures which focused attention on this area. Nevertheless, problems with high-strength steels in use today and lack of adequate understanding suggests that new research approaches should continue to be sought. One proposal was to model hydrogen distribution and effects using Nb-O₂, since this may be an effective way to study the surface/environment interactions, surface catalysis and reaction inhibition, and related embrittlement reactions using a system that is analytically easier to investigate. The

criticism raised was that insufficient evidence existed to adequately relate the reactions of the Nb-O₂ system to a low-alloy steel - H₂ system. However, it is better to have the temerity to present such ideas to a critical audience than to remain silent. Unfortunately, many were reluctant. This, of course, was expected and a suitably informed environment plus leadership by a few bold peers helped overcome it.

On the other hand, discussions of ongoing research and its possibilities were sometimes subject to the valid criticism, "You are ignoring significant parameters or phenomena." An example is some of the work stimulated by field failures on the mechanisms/hydrogen embrittlement of high-strength steels due to environmental reactions where the hydrogen pickup, in fact, came from incorrect plating procedures. Many failures in high-strength low-alloy-steel parts (7) have, upon careful analysis, been traced to hydrogen at trapped metal-coating interfaces during the electrolytic plating processes. This hydrogen migrates into the lattice and may not be removed during baking-out procedures. Elegant analyses of hydrogen embrittlement from environmental reactions at the surface and subsequent stress-corrosion cracking are simply irrelevant to this problem. Another example derives from the recognition, in recent years, that relevant environments for localized corrosion are significantly different from bulk-solution environments which are used for representative corrosion testing. Brown and co-workers demonstrated (8-10) that the so-called occluded cell or crevice could be simulated in the laboratory and obtained results far different from those predicted by ordinary reaction kinetics based upon bulk solutions. Solution concentrations often are unexpectedly high and the predominant crevice isolated hydrolysis reaction



results in acidic occluded cell media essentially independent of the bulk solution conditions and pH. Kruger (11) points out that new approaches to corrosion require consideration of this relevant chemistry in the isolated crevice. In addition, the relevant alloy composition and structure which recognizes localized differences in phases present, the relevant electrochemical mechanism and electrochemical potentials for experiments which accurately portray the initiating anion absorption process, and the subsequent study of relevant protective films all must be considered. Thus, localized corrosion processes require a whole new understanding of the phenomena to be studied. The appropriate use of Pourbaix-type potential - pH diagrams for describing corrosion process (12) also requires this understanding.

The natural reluctance of the "scientists" to appear naive in front of the "engineers and users" was intensified by an apparent real lack of information flowing to them about actual needs and in-service situations. Project Pacer Lime is an Air Force outdoor corrosion exposure test program which seeks to classify base environments according to their corrosion severity. The results are to be used to establish logistic and manning requirements and washing cycles in the corrosion-control program for the different Air Force bases. In conjunction with this effort, an interim Corrosion Severity Classification Index of base environments was developed from climatological data and educated guesses as to the relative importance of various environmental factors (13). For the past five years, outdoor atmospheric tests have been conducted at ten USAF bases located geographically in diverse environments. Metal-coupon test data have been obtained from these sites in the hope of relating exposure results to climatological data in order to develop an improved

*It is interesting to note that despite the large number of people working in corrosion in the USSR, the need for similar coupling activity was very evident to a recent visiting USA delegation (5).

Corrosion Severity Index with experimental validity. The collected data are currently being analyzed and it is premature to draw final conclusions. However, the task of clearly demonstrating how such results--even when complete--could be used to impact actual AF operations was not thoroughly accomplished and, as a consequence, there was considerable skepticism about this program. As a result the idea was superior to its execution. Without management attention, interest was lost as personnel were transferred in the five-year span. The replacement people often knew little of why the program was initiated and what was to be accomplished or of the resources necessary to complete the study. The collection of data suffered accordingly. The lesson is that a goal must be understood by the user as well as the initial planner, and this often requires improved definition of the goal.

Criticism of more applied activities often took the tone, "Who cares." An example is the development of improved anodized coatings for aluminum alloys by the use of fused-salt anodizing. The program itself was technically successful, and improved anodized coatings were developed (14). Using a nitrate-nitrite eutectic bath, an anodized layer was produced on high-strength aluminum alloys which was superior to the current commercial procedures such as sulfuric acid anodizing and surface-conversion coating treatments. Unfortunately, industry interest was in optimizing among several different existing anodizing treatments (sulfuric acid vs. phosphoric acid treatments, etc.) and not in the development of a new process. Investment requirements, prior history, inertia, and competitive processes have all resulted in no real "need" for application of the ongoing research effort.

It became apparent quite early that the current pacing activity in defining new directions for corrosion research and development was in identifying needs rather than in suggesting possibilities. All too often needs were expressed in such general terms that they could do little to stimulate--much less guide--fundamental research. Requirements such as "We need better test methods" or even "We need improved accelerated test methods," "We need better corrosion-resistant landing-gear alloys," "We need marine piping material development," or "We need better anodizing procedures for aluminum" not only are of little help, as indicated above, but also can be misleading.

Within the Air Force the term "window" has been used for several years to help illustrate needs and guide more applied activities. It is that part of the goal of a development or evaluation program that can be expressed as a realistic potential application or even a specific first-generation use of the technology. Defining a credible window involves answering difficult and sometimes embarrassing questions such as, "Even if I successfully meet these technical goals, who will use my product and for what application? Does it offer sufficient potential beyond the existing state-of-the-art to overcome inertia due to the normal reluctance to change or the risk of eventual failure? How will it fare against competing developments?" A suitable window provides a baseline against which the new technology can be evaluated. The possibility of actual near-term production and use stimulates enthusiasm in both program participants and potential sources of support. The problem, of course, is to define a specific potential initial application that will provide these advantages and also be sufficiently stimulating and generic that it can act as a vehicle for advancing the technology along a broad front toward potential uses well beyond the window selected.

When attempting to apply this approach to focused fundamental research, it is, of course, rarely possible to define specific windows for specific first-generation use. Not only does the time scale involved prohibit it but also, as has often been said, "If one can define the outcome of a fundamental research project, it may not be worth doing." As the research proceeds, the prediction of what is possible will change, and the goal or window must be modified. However, it is possible to express goals in terms of potential windows. One can postulate how new knowledge concerning corrosion mechanisms under different conditions would lead to the requirement for different methods of accelerated testing and then ask who would use the new tests if they were developed. This, of course, requires an intimate knowledge of the state-of-the-science in order to predict what might be possible and an alert awareness of how this can and does change with time. Such an evocative way of describing the potential for a particular area of research can help not only to generate support but also to provide the integrating emotional issue--the enthusiasm building--which will help overcome many of the institutional barriers to corrosion research mentioned previously. The goal provides a focus for interdisciplinary cooperation, enabling people from different fields to find a common ground for communication.

An example of current use of a potential window is work underway to develop realistic accelerated tests which correlate with service experience to rank aerospace materials in terms of their resistance to specific types of corrosion. It is expected that initial research efforts will define what is possible. For example, it appears that the important atmospheric pollutants for corrosion fatigue may be SO₂ for high-strength steels and nitrous-oxide compounds for high-strength aluminum alloys (15). The next step is to determine whether the effects of these pollutants can be accelerated in a realistic manner. If the results of these studies are promising, a specific window will be chosen to guide final reduction to practice, e.g., a test to predict the relative behavior of landing-gear steels. In this case one would have to consider how specific steels, heat treatments, protective coatings, hardware configurations, and actual usage patterns would influence development of a specific test method.

The authors have been involved in continuing attempts to stimulate the definition of windows or potential windows. These should come both from the recognized needs of the user and from those needs stimulated by the possibilities suggested by fundamental knowledge. Unfortunately, the effort required to derive these from generalized needs has been too sparse in the past, and the task is often very difficult. The requirement for realistic accelerated tests mentioned above is also an example of a window which, as often expressed, is too broad and vague to precipitate/initiate major research or reduction-to-practice efforts. It can present a limitless quagmire of opportunities. A real need is contained in the requests of Air Force operational commands to the laboratories and in similar requests from many industries to their respective R&D establishments. Upon examination, however, the goals are frequently obscure. Does one desire tests for large components, small components, or laboratory test specimens? Is the real environment known? Are field failure data available? Have mechanisms of field failure been identified? Unless clarified, these factors can drive the research in irrelevant directions or cause critical aspects to be ignored. Clearly one must divide the broad need into smaller subsets; many windows should result. A good example of this is the one given previously of corrosion-fatigue studies

being directed toward increasingly specific conditions as the research progresses.

An example of an oft-stated window which can be potentially misleading is in the request from Air Force users to develop nondestructive evaluation (NDE) for detecting corrosion under paints and paint condition. This has been interpreted as the need for evaluation of substructure deterioration and for residual paint protectiveness. Cosmetic appearance has been denigrated as a requirement by the laboratories since paint films are often protective even when they look decrepit. However, development of a method which ignored cosmetic quality would never be accepted by the field. Even if maintenance people could be convinced that appearance is unrelated to protectiveness, appearance is a legitimate concern of a field commander. A substantial R&D effort is now being planned on new NDE methods for corrosion in aircraft. The above example illustrates the importance of well-defined windows for such a program.

Despite such difficulties, success has been achieved in identifying windows and potential windows and using them to help define new directions for corrosion research and development. An excellent example of actionable windows stimulated by new possibilities came from presentations at the Corrosion Workshops (4) of the results of prior inhibitor research. New inhibitor systems based upon a borax-nitrate-nitrite system for steels with additions of small amounts of metasilicates, polyphosphates, and mercaptobenzothiazole for use with aluminum and other alloys have been explored in the laboratory. These were effective under conditions of crevice corrosion, corrosion fatigue, and stress corrosion in addition to general corrosion inhibition (16-18). Air Force maintenance people at the workshop described a new automated rinse facility at MacDill AFB in Tampa, Florida. The Navy had rinsed aircraft for some time, particularly aboard aircraft carriers and at places such as Jacksonville Naval Air Station where most of the missions are over salt water. Although the Air Force had not used rinsing previously, it was anticipated that it would be effective in removing dirt, soil, and evaporated salt, etc., resulting from operation and parking of aircraft near the coast. The wash water at MacDill AFB is considered to be hard (200 mg/l as CaCO_3). Thus, where entrapped on an F-4 aircraft scheduled for automatic rinsing, the water itself constitutes a corrosive medium.

The possibilities from the inhibitor research and the needs of this facility led to a firm window for evaluating and demonstrating inhibitor effectiveness in actual service. Inhibitors developed specifically for MacDill water as the initial part of a reduction-to-practice program are currently being added to the rinse water, and the effects upon reducing corrosion maintenance costs are being tracked. Initially a group of 50 F-4 aircraft was involved in the test program. Another reduction-to-practice effort has been initiated to develop and evaluate inhibitors for the bilge or lower bay areas of large cargo aircraft. Here again, a well-defined window to reduce the known cost of repairing corrosion damage around areas near latrines and galleys in aircraft such as the C-141A and C-5A emerged. Water collects in these areas due to drain holes becoming plugged. Inexpensive nontoxic inhibitor systems are required which can be easily applied and have a reasonably long life. These could be water-displacement compounds which currently have some problems related to limited life and toxic carrier agents, packaged inhibitors which have problems with caking and controlled solubility release, or special corrosion-inhibitive coatings which have toxic solvents, cost, and weight problems. Recognizing the inadequacies of current reduction-to-practice

approaches, research on new inhibitor systems to further expand the options is also being conducted (19).

A difficult-to-satisfy window that should stimulate focused need-driven fundamental research is in the area of paint strippers. Standard aircraft coatings are too difficult and too costly to remove; the process is slow, and the chemical strippers in current use do not meet current EPA/OHSA pollution safety and toxicity requirements. Since the Air Force requires complete depaint and repaint cycles on aircraft every five years, an important realistic window exists to use new technology; however, development efforts are limited by a lack of approaches. Research is required on topics such as solvent-paint reactions and the synthesis of waterborne paints and biodegradable nontoxic solvents which are non-corrosive to the metal surface. In the long range, the development of cross-linked high-performance polymers which have easily depolymerizable (by conditions not met in service) bonds for rapid removal of the paint film by mild chemical agents might be the optimum approach.

The authors have experimented with several formats for organizing the inputs to coupling in a manner which will aid in defining and displaying both the needs for additional input and the possibilities for profitable research or development programs. A recent version that has been found to be useful in a variety of forums and for areas such as processing and NDE science as well as corrosion is shown in Table IV. Its use will be described in a somewhat simplistic and provocative manner. The heading "General Problems/Needs" essentially provides only a table of contents. Predicting material behavior or the corrosion costs for a fleet of aircraft are well-known needs; but as has already been indicated, generalities such as these are not enough. The actionable inputs to coupling are emerging possibilities described in an evocative manner or needs described as well-defined windows or potential windows. The outputs are needs for focused research, the possibility of a development, or the requirement to better define windows or possibilities.

When a possibility and a window find a match in each other, there is a high probability that an applied reduction-to-practice program can be proposed and will find support and come into being (remember how carefully the need represented in the window was defined). The inputs leading to the previously described program on evaluating inhibitors for wash-rack rinse water are examples. Table IV provides an illustration of where matching a window with a possibility emerging from current knowledge/techniques has resulted in a development effort (indicated by *). The window was the desire of the Air Force to schedule major maintenance (the cost driver being corrosion repair) based upon need rather than fixed time intervals (isochronal) or number of flying hours. This is applicable to the C-141A and many other current inventory aircraft of average age exceeding approximately 10 years. The new possibility was the use of modern computerized analytical techniques to examine service maintenance data. The development program (20) analyzed all data believed to be relevant to corrosion damage and showed that costs are a function primarily of base location and its attendant environment rather than mission type and number of flying hours. The result, now being implemented, was to permit a more valid scheduling of programmed depot maintenance at extended intervals.

When windows can be defined but no possibilities are available, a stimulus to focused fundamental research becomes evident. The problem of developing standard test methods for stress corrosion of aluminum (21) to permit interlaboratory correlation of results is also illustrated in Table IV. Past

Table IV - Format For Organizing Information For Coupling

<u>Focused Research Needs</u>	<u>Reduction-To-Practice/ Development Possibilities</u>	<u>Windows</u>	<u>General Problems/Needs</u>
Simulated Atmospheric Testing/Environmental Accelerators Corrosion Mechanisms		Specific Aspects Of Acceler- ated Tests For Localized Corrosion, Crack Propagation, or General Corrosion	Predicting Materials Behavior
Relevant Mechanisms of Stress Corrosion		Standard Test Methods Usable By Different Laboratories	
	Computer Analysis of Main- tenance Cost Data*	Cost Models For Programmed Depot Maintenance, C-141A	Predictive Models
<hr/>			
	New Hydrogen Probe Development		Hydrogen Embrittlement Failure

FUTURE OUTLOOK

attempts to demonstrate such a capability by round-robin test programs have generally been unsuccessful. Additional round robins, without improved understanding of the sources of variance, would probably not be fruitful. The required focused research into stress-corrosion mechanisms--specifically to identify the controlling parameters for better test methods--remains to be done. A word of caution is in order; although an existing window can stimulate fundamental research, it can also result in restrictive goals if taken too literally. The previous discussion of "potential windows" applies. The need for more focused research against a subset of potential windows for accelerated testing is also indicated in Table IV. Before attempting the development of specific test methods against a specific window, it is often necessary to obtain more knowledge. As previously described, some effort is underway such as that using environmental pollutants as accelerators of the corrosion reactions. More effort is also required on corrosion mechanisms to indicate directions for realistic environmental acceleration of corrosion reactions by increasing reaction rates without substantially altering reaction mechanisms.

When possibilities seem to be emerging but no windows are forthcoming, there is a stimulus to better examine needs or to exercise creativity about potential new uses. As previously mentioned, despite much progress, hydrogen embrittlement is still suspected to be the cause of many field failures. Recent developments of new methods for hydrogen probe analysis with improved sensitivity and precision (6) constitute a reduction-to-practice possibility but specific windows for their use lack definition. As a result, it is difficult to obtain support for new R&D efforts. Perhaps these methods should be developed and applied in order to understand actual failures such as those in high-strength bolts.

Often, of course, the situation is not so simple as those implied above. Cases will arise where there is a need for both a better definition of the window and for an improved knowledge base to support a reduction to practice. This has been a difficulty with the Pacer Lime Project discussed previously. In addition to poor definition of the window, there was insufficient definition of research requirements. No stressed or scratched specimens were used; no painted specimens were used; and personnel were generally untrained. The reduction to practice suffered as a result.

The discussion to this point has been concerned with development activities or need-driven fundamental research. Defining new directions for truly basic research has not been considered. However, the authors would like to suggest that the better definition and pursuit of need-driven work will have an inevitable influence upon the knowledge-driven work. The latter tends to focus on simple experimental conditions, with only one parameter being varied at a time. By exploring complex, multiparameter situations, the need-driven work may often encounter new phenomena; and the lure of understanding these phenomena can provide a refreshing stimulus. For example, the chemistry of conditions in a crevice can involve high, non-equilibrium salt-concentrations and possibly unusual diffusion rates (11). Also, the focusing of paint-degradation studies to relate directly such factors as permeability and ion diffusivity to corrosion-initiating processes appears to be leading to new fundamental understanding of thin-film behavior and diffusion through thin-film barriers (22).

The outlook for corrosion research and development should be bright. Society's need for such activity is clear. A broad range of new research tools and approaches from many disciplines can be brought to bear including new sophisticated methods for surface analysis in the study of real (service-failure related) degradation mechanisms (19,22). Too often the use of tools such as Auger analysis, ESCA, the ion-probe, etc., remains with the more esoteric elements of the research community. Another possibility is the use of surface-chemistry modification by ion implantation to improve corrosion resistance without alteration of substrate properties--an opportunity-driven possibility. Some initial work in this area has been done, and the results are encouraging (23). It is possible to scale up such laboratory procedures as demonstrated by industrial ion implantation of semiconductors on a mass-production scale (24).

Finally, as discussed earlier, effective coupling between corrosion science and technology and use--although often difficult--can be encouraged. An obvious key to this will be the horizontal and vertical interdisciplinary individuals who can describe possibilities in evocative terms, who can help to define windows, and who can convert the complex scientific problems presented by realistic windows into terms and components significant to more specialized investigators. Attendees at this symposium and future readers are challenged to accept some of the responsibilities of such a role.

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ABSTRACT

Navy sponsored studies on the problem of sea salt-induced "hot corrosion" in ship propulsion gas turbines have brought together new data and concepts which advance the understanding of metal-salt reactions under high temperature conditions. These studies show the importance of applying basic physico-chemical concepts to the systematic study of molten salt corrosion. In this review the relevant principles and techniques are presented and their application is illustrated through a discussion of gas turbine corrosion.

MOLTEN SALT CORROSION was first recognized as a problem of serious economic consequence with fireside boiler tube corrosion in coal-fired steam generating plants in the 1940's. It has since reoccurred as troublesome "hot" corrosion in gas turbines, especially for those operated in marine or other salt-contaminated environments, and is now projected as a threat to many of the systems (coal gasification, MHD, fluidized bed combustion) proposed for the new energy technology. Molten salt fuel cells and batteries, salt processing baths, solar energy storage by molten salts, and many other energy relevant systems are also candidates for salt-induced corrosion. In future years as the quest for fuel efficiency forces us to ever higher temperatures and larger plants (with huge capital investments), molten salt corrosion will become potentially even more critical, and we may anticipate a new level of need to understand, and to develop materials and means to combat, corrosion by fused salts and slags.

Gas turbines represent, in a sense, a middleground between the old and new energy technologies and serve to give some insight into the economics and problems involved with salt-induced corrosion. There are many advantages in using gas turbines for ship propulsion, and the U. S. Navy is currently adding several classes of gas turbine powered ships (to cost in excess of \$30 billion) to the Fleet. Because of the cost, and the strategic role these ships will play, there is great Navy concern to insure that their performance will not be compromised by sea salt derived hot corrosion of the gas turbine engines. Similarly, industry and local governments are making heavy investments in gas turbines for electricity generation and non-aviation mechanical power, with more than \$8 billion being spent worldwide for new installations alone in the period 1976-1979. Substantial difficulty with hot corrosion has been observed with many installations. It has been estimated, for example, that more than 50% of repair on electric utility gas turbines is necessitated by salt related corrosion, with reblading (at costs of \$70,000-100,000) being required in some cases after

less than 3,000 hrs operation (1).^{*} Corrosion costs of this magnitude may pale into insignificance in the future however when, as an example, coal gasification or liquefaction plants, some of which are projected at \$1 billion or more each, come under attack.

Molten salt corrosion research is sponsored by several government and non-profit agencies, including notably the Department of Energy (DOE), the National Aeronautics and Space Administration (NASA), and the Electric Power Research Institute (EPRI), as well as the Navy. The gas turbine engine manufacturers and other industrial firms, and certain university groups, have also carried on substantial research. As a result of this, and of earlier and foreign work, there is a considerable literature in the form of reviews, books, and conference proceedings concerned with fused salt corrosion in the different areas such as fireside corrosion (2,3), gas turbine hot corrosion (4,5,6), coal conversion (7), and MHD (8,9). However, the extent of research is not nearly so great as in aqueous corrosion study, and it has suffered in some degree from being "compartmentalized", with the broad view of molten salt physical chemistry not always appreciated.

Our purpose in the present paper is to provide a brief review of certain fundamental aspects of molten salt physical chemistry which essentially represent a central theme for all areas of molten salt corrosion study. Short descriptions of some of the current instrumental methods in fused salt research will also be given, and the paper will close with examples of application in Navy sponsored gas turbine hot corrosion research.

I. BASIC PROPERTIES

A. PURE SUBSTANCES - Only a relatively small number of substances is involved in molten salt corrosion. These include first the salts themselves: NaCl, Na₂SO₄ and K₂SO₄ in turbine and fireside corrosion, K₂SO₄ and K₂CO₃ in MHD where they are used as seed materials to make the hot gas conductive, carbonates in various industrial processes including fuel cells and to a minor extent, fluorides and phosphates. Because Na₂SO₄ is formed so easily from ever-present NaCl, O₂ and sulfur in fuels, by far the largest research effort has been concerned with this salt. Gases which affect molten salt corrosion are those which are present either as reactants or products in salt formation and decomposition, mainly SO₂, O₂, and SO₃, and to some extent salt vapors. Finally we have the metals and ceramics whose corrosion is of concern and their corrosion products, primarily oxides and sulfides. Although not strictly salts and thus not part of this review there is an area of research involving corrosion by slags (10), i.e., silicate melts which arise from impurities in coal. Fortunately the list of materials involved in corrosion processes is not long because the complexities possible are difficult enough to unravel so that the task is not nearly complete after more than two decades of effort.

There are two general approaches to the study of corrosion: thermodynamics and kinetics. By far the largest effort has gone into the first of these.

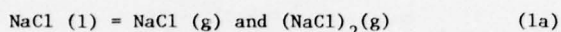
1) Thermodynamic Data - Although corrosion processes are generally far from equilibrium, e.g., gases pass through the system, condensed phase reactions produce concentration gradients, thermodynamics in many cases is the most reliable guide as to what may

^{*} Number in parentheses designate References at end of paper.

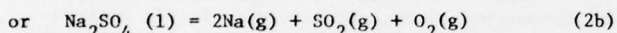
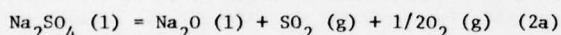
be expected to occur in a corrosion system. This is because it frequently predicts what the corrosion products are likely to be and because some regions of the system, particularly the salt-substrate interface, may be close to equilibrium. Moreover, even for systems not at equilibrium, thermodynamics offers much guidance as to what may be expected when the system is displaced from equilibrium.

Although not all the data required are equally reliable, nevertheless there exists a body of critically evaluated data of all the standard thermodynamic functions over a wide range of temperature in the JANAF tables (11). More specialized compilations are also available (12,13). Thus, a lack of knowledge of thermodynamic data for pure substances is rarely an impediment to corrosion research.

2) Vaporization and Thermal Decomposition - When salts are heated they vaporize and/or decompose. Examples of vaporization are



In decomposition the salt "molecule" breaks into fragments. Perhaps the most important single decomposition reaction in molten salt corrosion is



since Na_2O is also relatively unstable. These processes are important because the gaseous products may themselves be corrosive (NaCl , SO_2) or because equilibria such as (2) alter the acid-base characteristics of the melt (see below) and thus affect solubilities and reaction paths.

Vapor pressures of alkali halides are easily calculated from existing thermodynamic data.

Decomposition equilibria for the major classes of oxyanion salts (sulfates, carbonates, nitrates, nitrites, and all the oxyhalogens) have been calculated (14a,b,c,d), but the equilibrium constants must be carefully applied when the salt is liquid. Thus, for reaction (2a) the equilibrium constant is

$$K = a_{\text{Na}_2\text{O}} \cdot P_{\text{SO}_2} \cdot P_{\text{O}_2}^{1/2} \quad (3)$$

since in pure Na_2SO_4 , $a_{\text{Na}_2\text{SO}_4} = 1$, and the oxide activity in the melt is clearly a function of gas composition. Oxyanion salt molecules in the vapor state have only recently been discovered (14c,15,16,17) and thermodynamic information on them is still scarce.

The subject of thermal decomposition has frequently been considered from its obverse aspect: thermal stability. Does a particular salt exist at a certain temperature? For a given salt this problem can be considered in terms of eq. (2), but it is interesting that salts of a particular oxyanion, e.g., SO_4^{2-} , differ greatly in the temperature at which decomposition becomes observable. It is well known that the higher the polarizing power of the cation the less stable is the anion. For example, Cs_2SO_4 is the most stable sulfate and SnSO_4 the least stable. A quantitative theory of this phenomenon applicable to all oxyanion salts which decompose endothermically to an oxide and a gas has been developed (18).

The kinetics of molten salt vaporization and decomposition is a field still in its infancy although it is of importance for corrosion, since in real systems the equilibrium vapor is rarely present and vaporization usually occurs into a fast moving gas stream. For a substance vaporizing into an

equilibrium vapor the rate is given by the Hertz-Knudsen-Langmuir equation (19)

$$J_e = (2\pi)^{1/2} P(M/RT)^{1/2} \quad (4)$$

where P is the equilibrium vapor pressure and M the molecular weight of the effusing species. When more than one species is involved, as in decomposition, eq. (4) must be appropriately modified. For vaporization into a vacuum or inert gas the flux may be less than J_e and is expressed in terms of vaporization coefficient α :

$$\alpha = J/J_{e,eq}, \quad \alpha \leq 1 \quad (5)$$

Vaporization theories are thus theories of α . Theoretical aspects of this subject have been extensively discussed (20).

Experimental studies of vaporization and decomposition have largely been confined to solids (21,22) but recently there have been some thermodynamic studies of molten sulfates (15,16,17,23). Kinetic studies have largely been limited to alkali halides (24) and a study of Na_2SO_4 is in progress (25). Indications are that $0.1 < \alpha < 1$ for these salts.

B. SALT MIXTURES - Salt mixtures enter corrosion research in two ways: (a) the technology may require a molten salt mixture, e.g., binary or ternary salt melts in fuel cells, or (b) a multicomponent melt may be formed as the result of corrosion processes. For example, in the corrosion of alloys by Na_2SO_4 , the (liquid) sulfides of several alloy components may form, or vanadate impurities in the fuel may dissolve in the sulfate phase. The question of primary interest is the range of temperature and composition over which solid and liquid phases are formed. This information is largely embodied in phase diagrams. A large collection of these has been compiled by Voskresenskaya (26) which is readily available. A continuing series called "Phase Diagrams for Ceramicists", issued by the National Bureau of Standards (27) also includes systems containing oxides and silicates.

Phase diagrams also constitute a frequently overlooked source of thermodynamic data on melts. In many cases it has been assumed that salt melts behave ideally, i.e., obey Raoult's law. Only rarely has this assumption been tested experimentally and it may lead to erroneous interpretations of reactions and solubility parameters. Methods for using solid-liquid equilibria for activity calculations are well established (28).

C. SOLUBILITIES

1) Gases - Gases commonly dissolve in melts and this solubility is usually expressed in terms of the Henry's law constant

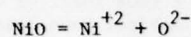
$$X_i = K_h P_i$$

where X_i represents the gas solubility, P_i the partial pressure, and the units of K_h are consistent with X_i and P_i .

Gases dissolved in melts are of importance to corrosion since they may affect reactions occurring at the melt-substrate interface, or alter the melt composition, particularly when they involve an equilibrium such as (2). For example, NaCl dissolved in Na_2SO_4 affects the corrosion of alloys (29); O_2 dissolved in melts containing the oxide ion (O^{2-}) reacts to form peroxide (O_2^{2-}) and/or superoxide (O_2^-), (30,31). The corrosive properties of these species may differ from that of the original O^{2-} ion. Various gas solubility data in molten salts have been collected in the Molten Salt Handbook by Janz (32). The recent work by Andresen (33) on the solubility of SO_2 and O_2 in

Na_2SO_4 is also of considerable interest. Flengas and Block-Bolten have discussed the solubility of reactive gases in great detail (33a).

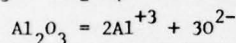
2) Condensed Phases - The major species whose solubilities are of interest are oxides and sulfides. For example, the course of a corrosion reaction may depend on whether a protective oxide is insoluble in a molten salt. Although the subject is important, very little work has been done on it. In older studies (32) the oxide solubility was determined by equilibrating the solid with the salt and analyzing the latter. Yet it is clear that the solubility of many oxides depends critically on the basicity of the melt. For example, a simple oxide such as NiO dissolves by a reaction which produces ions,



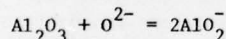
to which the solubility product principle applies,

$$K_{sp} = [\text{Ni}^{+2}] \cdot [\text{O}^{2-}]$$

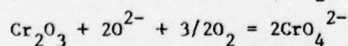
so that the metal concentration in the melt depends on the O^{2-} concentration. A few such solubility products have recently been determined, primarily by potentiometric titrations (34,35). In some cases the solution reaction may depend on the basicity of the melt, as has been shown by Stroud and Kapp (36) for Al_2O_3 and Cr_2O_3 in Na_2SO_4 . In acid solution,



whereas in basic solution,

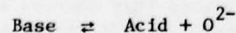


Studies of oxide solubilities have been greatly facilitated by the development of electrodes reversible to oxide ions in the melt (see below), but no such electrodes are yet available for sulfide ions in molten salts (although they exist for aqueous solutions). As a result, the solubility of sulfides has not yet been studied. A means for following the S^{2-} concentration in the melt would aid our understanding of sulfate corrosion since sulfides formed by reaction of SO_4^{2-} with metals may be reoxidized by O_2 . Thus it appears that "solubility" may be a complex phenomenon, not always strictly distinguishable from chemical reaction, and that the concentration of a metal appearing in solution depends both on other species dissolved in the melt and on the composition of the gas phase. A well-known example is the solubility of Cr_2O_3 which is very small in the absence of O_2 but indefinitely large in the presence of O_2 :

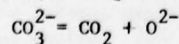
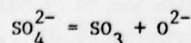


The CrO_4^{2-} ion simply dissolves in the melt.

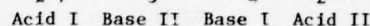
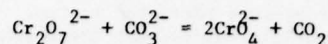
D. ACID-BASE PROPERTIES - Ever since the work of Lux (37) and Flood (38) it has been customary to consider oxyanion salts in terms of an acid-base equilibrium in which the O^{2-} ion plays a role quite analogous to the hydrogen ion in aqueous solution:



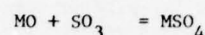
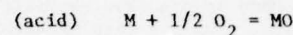
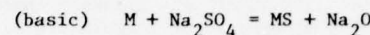
For example



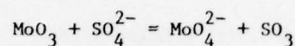
Justification for this concept comes from many observations that these equilibria participate in acid-base reactions, e.g. (39)



The importance of this subject for corrosion lies in the fact that the shifting of various equilibria in the presence of a metal or metal oxide will affect the reaction mechanism. The solubility of oxides was discussed in the previous section. As an example of metal reactions we cite the corrosion in Na_2SO_4 :



SO_3 may be present in the gas phase or be produced by the reaction of an acidic oxide with SO_4^{2-} , e.g.



Further examples of the importance of acid-base properties to corrosion can be found in the review by Imman and Wrench (39).

E. CHEMICAL REACTIONS - From the above discussion it is clear that at high temperatures, even when only a few substances are present, the number of possible interactions is quite large. Similar conclusions had been reached much earlier about corrosion in aqueous solutions. As a result of this realization, Pourbaix in 1948 devised a graphical method for summarizing the thermodynamic (frequently electrochemical) data applicable to a given corrosion system. Such a Pourbaix diagram enables one to visualize easily the stability regions of various substances as a function of solution and/or gas phase composition. There now exists an extensive collection (40) of such diagrams applicable to aqueous corrosion.

The situation for molten salt corrosion is more complicated because each salt forms its own "system." Nevertheless, the utility of the method is so great that it has gradually been adapted to molten corrosion. Littlewood (41) was probably the first to do so, applying the Pourbaix concept to the corrosion of metals in alkali halides in the presence of oxygen. Such a diagram shows whether a particular metal will be stable, or react to form the soluble halide, or an insoluble oxide. The method has now also been extended to slags (42) and to molten carbonates (43).

Corrosion in molten sulfates is probably more complicated than the above cases because insoluble sulfides may also be formed by reduction of SO_4^{2-} . Nevertheless Quets and Drescher (44) have developed a method applicable to constructing graphical representations of metallic corrosion in Na_2SO_4 based on a consideration of the phase rule and known equilibrium constants. An example of the method is shown in Fig. 1 for the Ni-S-O system. In this volume diagram the axes are temperature, P_{O_2} , and P_{S_2} . The stability region for a single condensed phase appears as a volume, for two condensed phases as a plane, for three condensed phases as a line, and for four condensed phases as a point. An isothermal cross section of this diagram at 1200K (plane A-A) is shown in Fig. 2. The stability region for a single condensed phase is now a plane, etc. Quets and Drescher (44) also show how, by also considering the Cr-S-O system, the corrosion of nickel-chromium alloys can be predicted. The utility of the diagrammatic method has proved so attractive that it has now come into widespread use.

Nevertheless, thermodynamics is not the only determinant of corrosion reactions. Corrosion systems are frequently not at equilibrium and reactions which are thermodynamically rather unfavorable may still

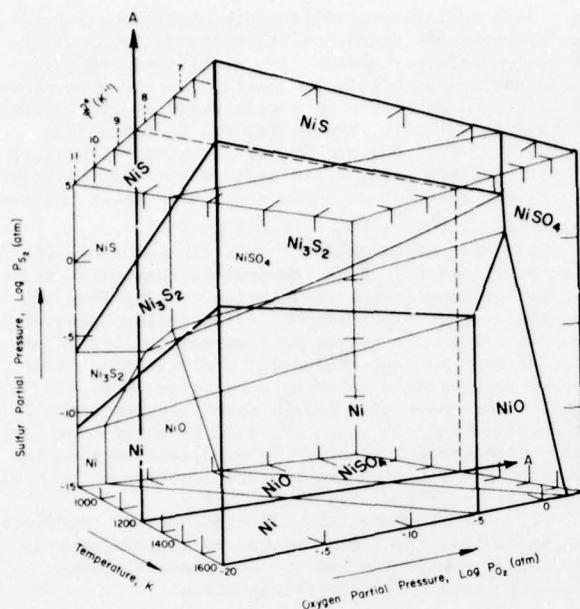


Fig. 1 - Predominance volume diagram for Ni-S-O system at temperatures between 900 and 1600K *

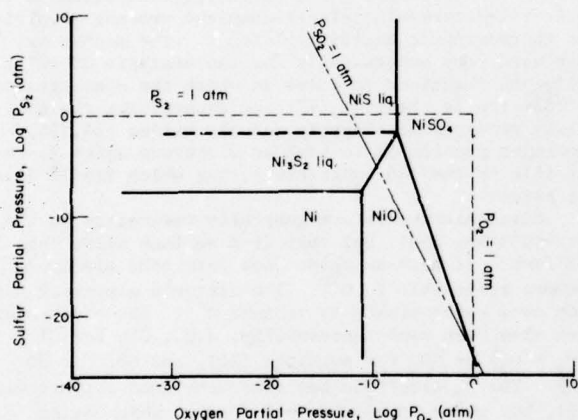
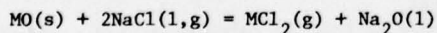
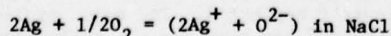


Fig. 2 - Predominance phase diagram for Ni-S-O system at 1200K (Section A-A from Fig. 1) *

proceed if the kinetics are favorable. The most common example is the distillation of a volatile product. For example, reactions of the type



where M is a structural metal like nickel or cobalt, are thermodynamically quite unfavorable, but are very effective in halide corrosion because the chloride product is very volatile (45). (Since MO is very stable it is readily formed by atmospheric oxidation of the metal.) A reaction may also be driven by alloy formation. For example, silver corrodes in NaCl by two simultaneous reactions,



* Footnote: Figs. 1 and 2 reprinted by permission of the American Society for Testing and Materials, Copyright.

The first of these reactions requires an O_2 atmosphere and comes to equilibrium. The second reaction which is thermodynamically very unfavorable is driven by formation of a sodium-silver alloy which lowers the sodium activity (46).

In contrast to the above discussed aspects of corrosion, which are the gross features, there are the finer details of reaction mechanisms, particularly the initial steps. Metallic corrosion can be characterized as a heterogeneous electron transfer reaction and thus is ideally suited to electrochemical techniques. Reactions of this type can be described by a series of steps (47).

- Diffusion of reactants to the surface
- Adsorption of reactants
- Electron transfer
- Desorption of products
- Diffusion of products away from surface

Any of these steps may be rate-determining. Modern electrochemical techniques, which involve a very sophisticated manipulation, both experimental and theoretical, of the variables voltage (driving force), current (reaction rate), and time, are uniquely capable of analyzing such events on a very short time scale. Curiously, although these techniques have been widely applied to analytical problems (48), electrodeposition (49), synthesis, and reaction mechanisms (50) in molten salts, the application to corrosion problems seems to be largely missing and would provide a fertile field for exploitation and exploration.

II. EXPERIMENTAL TECHNIQUES IN SALT CORROSION RESEARCH

The realm of interest in molten salt corrosion centers principally on the corrosion site itself, i.e., on processes occurring at the solid (metal or ceramic) - salt interface. Related problems largely involve the melt and solid phases at either side of the interface, their composition and changes in composition as a result of corrosion. In some instances, the gas phase materially affects these phenomena and then becomes an object of study in its own right.

The number of techniques which have been used in fused salt corrosion study is relatively small. Most of them are well known in other connections, except possibly the more esoteric electrochemical approaches, and will be discussed only briefly to indicate their utility.

A. THERMOGRAVIMETRY - Thermogravimetry involves monitoring weight change under carefully defined conditions at fixed or varying temperature to establish, e.g., rates of corrosion or thermal decomposition. For corrosion rate determinations, periodic weighings of specimens exposed to bulk melts or with salt coatings is often used. A preferred procedure is to employ an automatic recording balance to continuously follow weight change as the specimen, usually as a suspended salt-coated coupon, is exposed to the high temperature environment. Caution is always required in interpreting thermogravimetric corrosion data, since oxide spalling, salt or corrosion product volatilization, or metal and oxide dissolution in the melt (when employed) can offset the increase in weight normally expected with corrosion.

Thermogravimetry has also been very useful for the determination of salt vapor pressures and vaporization kinetics. For salts vaporizing or decomposing by a process for which the vapor composition is known, the weight loss leads to a precise determination of partial pressure through the well known Knudsen techniques. Thermodynamic measurements on several halides, sulfates, and carbonates important in molten salt corrosion have been reported. The technique can also be applied to vaporization/decomposition kinetics but most of the literature involves solid salts. Work on molten

salts is almost non-existent although a program in this field has been started at our laboratory. These topics are described in Section IB.

B. MICROSCOPY AND X-RAY ANALYSIS - These represent the basic tools for identifying corrosion phases and structure to help deduce the mechanism of metal-salt interaction. Traditional metallurgical light microscopy continues to be important and can contribute unique information. Polarized light microscopy, for example, can be used to identify salt crystals interdispersed in the corrosion phase, and hot stage microscopy has provided valuable insight, showing a lateral attack of molten sulfate under the surface oxide layer, in studies of metal corrosion by Na_2SO_4 at 900°C.

Scanning electron microscopy is also much used and affords an approximately 500X advantage in depth of focus, and 25X advantage in resolution over the metallurgical light microscope. Many SEM's presently are fitted with energy dispersive X-ray analyzers which, by using a solid state detector to measure the characteristic energies of the X-ray photons generated by impingement of the electron beam, can give an analysis of the elemental composition of the specimen.

"X-ray maps" (Fig. 4) produced by feeding the signal for a particular element into the cathode ray tube circuitry are popular for depicting elemental distributions. The more specialized electron beam microprobe is still required for detection of light elements such as oxygen.

X-ray diffraction can serve to identify phases produced within the metal, i.e., sulfides etc. resulting from inward diffusion of various species, oxides and other phases in the corrosion product, and compounds which may occur in the salt itself, e.g., pyrosulfates. Diffraction analysis is particularly valuable when slags and complex salts are to be characterized.

Other X-ray/electron interaction techniques such as Auger electron spectroscopy and X-ray photoelectron spectroscopy, which can give information on the oxidation state of the different species, may ultimately prove beneficial, especially if available in a high resolution scanning mode, but little work has been so far reported.

C. GAS ANALYSIS - The composition of gases in the vicinity of the corrosion site frequently influences the nature of the corrosion process. Oxygen is obviously important, but in general the problem is with low concentrations of chlorides or other corrosive gases such as SO_2 which may be reversible decomposition products of the salts themselves.

By far the greatest work has been concerned with the analysis of SO_2 and SO_3 in stack gas, both from the air pollution and fireside corrosion aspects. Although attempts have been made to develop "on-line" instrumental techniques, wet chemistry procedures remain most used, with collection of the SO_2 by controlled condensation, and of the SO_3 by absorption in hydrogen peroxide being recommended (51). Equivalent tests for total NO_x are available, but more specific procedures (or mass spectrometry) able to distinguish between the different nitrogen species would be required for a serious study of the decomposition gases of molten nitrates.

An analysis of HCl or vaporous NaCl in the gas phase is not usually undertaken in molten salt corrosion situations although it is now clear that NaCl has deleterious effects in sulfate induced hot corrosion at partial pressures well below the condensation pressure (29), and perhaps even down to the ppm range (52). Difficulty with sampling of the condensable chlorides might be encountered, but an analysis of the chloride concentration in the gas could prove beneficial in many circumstances.

High temperature solid state electrodes represent an important new means for analyzing gas composition in molten salt corrosion. The stabilized ZrO_2 electrode has proven highly successful for the measurement of O_2 pressures over a very wide range of temperatures and pressures (53). Recent reports indicate that analysis of SO_2 , CO_2 , and NO_2 at elevated temperature may be possible using solid state electrodes based on reversible reaction of these gases with their cognate salts, i.e., SO_4^{2-} , CO_3^{2-} , and NO_3^- (54).

D. MASS SPECTROMETRY - This technique has found wide application in high temperature chemistry, primarily for identifying the species arising from the vaporization/decomposition of solid phases, frequently ceramics (20). In molten salt corrosion, its major use has been in determining the composition of salt vapors from various relevant pure salts, e.g., Na_2SO_4 (16). There have also been limited studies seeking to characterize the gases produced by molten sea salt, and to isolate and identify intermediate species resulting from the high temperature reaction of NaCl with metal oxides, especially Cr_2O_3 (55).

E. ELECTROCHEMISTRY - Electrochemical techniques can be divided into equilibrium and kinetic methods. The former consists primarily of classical potentiometry based on the Nernst equation

$$E = E^\circ + \frac{RT}{nF} \ln a_i \quad (6)$$

where n is the number of electrons participating in the potential-determining electrochemical process involving the thermodynamic activity of ion i. The method has been used very successfully for the analysis of melts, following reactions in melts in which the concentration of some ion is changing (47) and determining the solubility products of slightly soluble oxides (34,35). The major problem is to find an electrode which is reversible to the ion under study, but which itself does not react.

Metal electrodes are generally reversible to the corresponding ions, but only if a surface oxide does not form. If such an oxide does form, the electrode becomes reversible to O^{2-} . The zirconia electrode has been used successfully to measure O^{2-} . Gas electrodes have also been used successfully, e.g., Cl_2 for Cl^- , ($\text{SO}_2 + \text{O}_2$) or SO_3 for sulfates (36), and CO_2 for CO_3^{2-} (56). The O_2 electrode has also been used extensively (57), but there is some question as to which oxide species (O^{2-} , O_2^{2-} , O_2^-) it is reversible to. Employment of any of the above indicator electrodes requires a stable reference electrode. The construction of such electrodes has been described (58). They are largely based on Ag/Ag^+ in a ceramic or glass envelope. More recently an excellent reference electrode useful for all melts in which Na^+ is the major cation has been developed (59).

The number of kinetic techniques, e.g., various forms of voltammetry, chronopotentiometry, has grown very large. In all cases the measured or controlled variables are potential, current and time. They have been extensively described (60), primarily for electro-analytical applications, including applications to molten salts (61), and also for such parameters as ionic diffusion coefficients. They are also potentially very useful in studying the individual steps in the corrosion process but this application seems to have been largely neglected. The major application to corrosion research has been for the evaluation of alloys in molten salt environments (62,63).

III. APPLIED MOLTEN SALT CORROSION RESEARCH

Recent research in the Navy program for improved marine gas turbine materials illustrates how important

an understanding of high temperature metal/salt chemistry can be in molten salt corrosion. This work has been conducted by the engine manufacturer and other industry and Navy laboratories. When it began, the general opinion (although not held by all) was that condensed Na_2SO_4 was the essential corrodent in gas turbine hot corrosion; that NaCl passed through the turbine as vapor and had no sensible effect, except possibly as a source of Na_2SO_4 produced by reaction with SO_2 in the combustor; that the sulfur content of the fuel was non-critical, at least up to 1%; and that there should be little corrosion (for lack of a molten phase) if the blade temperatures were held below the Na_2SO_4 Mp, 1623°F. It is now known that all of these premises are wrong including, in particular, the last point. References are still made to "holding the blade temperatures below 1500°F to prevent corrosion", but in truth, for reasons to be seen below, this is no guarantee against hot corrosion. It was in fact the observation of "anomalous" hot corrosion during low power sea tests (blade temperatures at 1200-1400°F) which largely motivated the Navy-sponsored investigation.

The investigation has demonstrated the necessity for considering not just a single component but the total system; in this case, the reactions of the salt species NaCl, Na_2SO_4 and SO_3 with the turbine metal (Ni, Co, Cr, Al) oxides at 1300°F. The cause of low power hot corrosion, as it has been revealed, is not Na_2SO_4 directly, but rather the formation of turbine metal sulfates, especially CoSO_4 and NiSO_4 , which subsequently combine with Na_2SO_4 to yield mixed sulfates melting as low as 1100°F, as shown for the CoSO_4 - Na_2SO_4 system in Fig. 3.

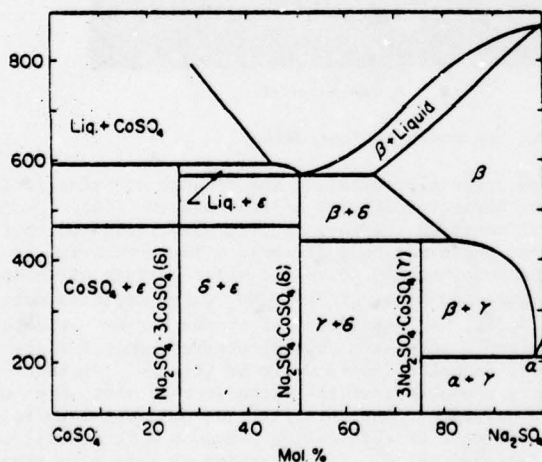
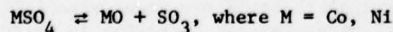


Fig. 3 - CoSO_4 - Na_2SO_4 system (K. A. Bolshakov and P. I. Fedorov, Zhur. Obshchei Khim. 26, 349 (1956))

The metal sulfates are produced by reversal of the dissociation reaction



High SO_3 pressures are required for reversal of this reaction at temperatures above 1500°F, but at 1300°F, representative of low power blade temperatures, as little as 10^{-4} (for CoSO_4) or 10^{-3} (for NiSO_4) atms of SO_3 are sufficient to produce the sulfate (14). This level of SO_3 is readily obtainable by combustion of the up to 1% sulfur allowed in marine gas turbine fuel. Thermodynamic calculations from the engine manufacturer's laboratory indicate further that the metal

sulfates are stabilized through dissolution in Na_2SO_4 , allowing molten mixed sulfate formation at even lower SO_3 pressures.

Other studies have shown that NaCl vaporizes slowly from metal surfaces at 1200-1300°F, especially when occurring as mixed deposits with Na_2SO_4 , but reacts rapidly with SO_3 , yielding Na_2SO_4 with the liberation of chlorine (a process which may have corrosion effects in itself (64)). Thus, the absence of chloride in blade deposits is not necessarily evidence, as previously assumed, that NaCl vapors never condense or dissolve in the surface salt film, or that chloride-rich particles never strike on the blade surface, but could be equally well the result of the rapid reaction that NaCl undergoes with SO_3 . However, while the reactions of NaCl are clarified, the major indication is still that low power corrosion is intrinsically linked with the SO_3 /turbine metal oxide reactions and the resultant formation of molten mixed sulfates.

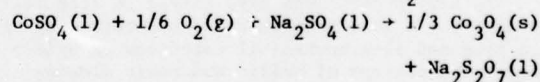
The role of the molten sulfate is not totally defined, but it appears to act in some instances as a stable liquid reaction medium when the SO_3 pressure is above the equilibrium value, and in others as a source of SO_3 itself through partial dissociation brought on by thermal fluctuations or side reactions. The corrosion pit in Fig. 4 was produced, for example, by decomposition of a deposited layer of 50 mol-% CoSO_4 - Na_2SO_4 at 1400°F.

Fig. 4 shows the characteristic morphology resulting from low power hot corrosion of "CoCrAlY", a Co-based alloy applied as a corrosion-resistant coating on turbine blades. The distinguishing features are, 1) the occurrence of little de-alloying of metal or sulfide formation in advance of the corrosion front (in contrast to hot corrosion at 1600°F and above), and 2) the transport of cobalt from the pit body, while chromium is left largely in place. The immobility of chromium is thought to be due to its low solubility in SO_3 -rich, acidic sulfates (36). The transport of cobalt is not fully explained, but a theory under development in the engine manufacturer's laboratory considers that cobalt is first oxidized at the corrosion front (probably by SO_3 since O_2 transport through molten sulfates is very limited) and then solubilized and transported by the following reactions where SO_3 occurs as pyrosulfate:

At the bottom of the pit



Then at the pit outer edge (high P_{O_2})



The transport of aluminum is more variable, although evidently it occurs in some cases (Fig. 4), and may depend on the exact P_{SO_3} 's achieved, since while mixed molten eutectics of $\text{Al}_2(\text{SO}_4)_3$ - Na_2SO_4 are possible, they require a higher P_{SO_3} than either cobalt or nickel.

Synergistic interactions between the various metals may also act to facilitate their dissolution. As an example, nickel oxide is soluble in CoSO_4 - Na_2SO_4 under lower SO_3 pressure than required to dissolve NiO in Na_2SO_4 , i.e., to form a liquid NiSO_4 - Na_2SO_4 phase. There is evidence suggesting that a similar effect may exist between cobalt and aluminum, although the exact conditions for its occurrence have proven difficult to define.

Some aspects of the data needed to answer questions such as the above pertaining to dissolution of

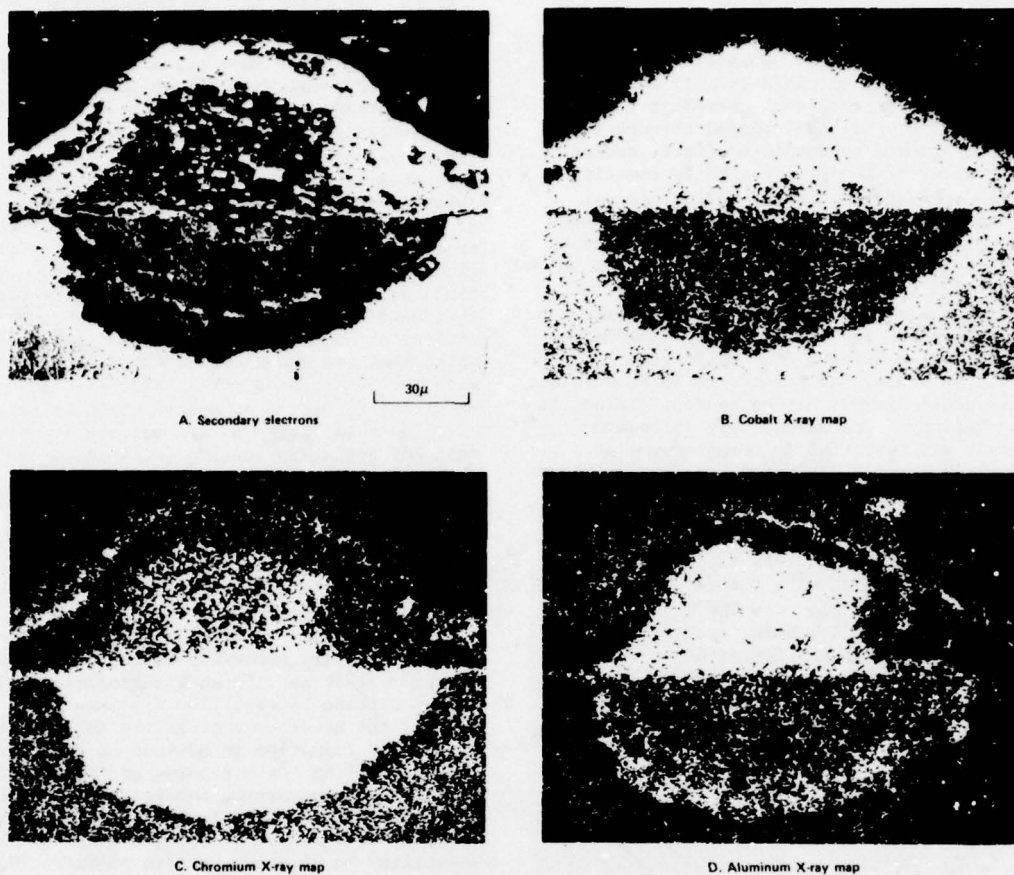


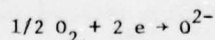
Fig. 4 - Characteristic morphology of low power hot corrosion

mixes of metals in sulfates would be contained in the ternary phase diagrams for the various sulfate systems. Unfortunately there are very few presently available which represent an appropriate combination of the corrosive salts and potential metals of construction. The development of relevant ternary phase diagrams, taking account of the SO_3 over-pressure and temperature functions, is an area of research which could ultimately be of great benefit in hot corrosion and other molten salt corrosion problems.

The Navy program has also served to accentuate the need for a more comprehensive understanding of acid-base and electrochemical reactions in molten sulfates. The concept of acidic and basic fluxing (dissolution) of protective oxides has been known for some time (65), but quantification of the theory is still largely lacking, except for the recent study on Cr_2O_3 and Al_2O_3 solubility as a function of O^{2-} concentration in Na_2SO_4 (36). The determination of metal oxide solubilities in general requires further study, particularly since, as in the last case with Cr_2O_3 , dissolved oxygen may have effects on the oxide solubility which are not yet explainable. There is a need also to verify that bulk oxides, as normally used in solubility measurements, do not react differently than oxides still in contact with the metal, as seen in "reductive dissolution" of iron oxide films on steel in aqueous corrosion.

Concerning electrochemical reactions, it has been thought that cobalt and perhaps other multi-valent transition metals form stable complexes, $[\text{M}(\text{SO}_4)_2]^{2-}$,

which are easily oxidized and reduced and thus facilitate charge transfer in molten sulfates (66). Certain experiments in the Navy program have indicated that indeed there may be a difference in corrosivity between $\text{CoSO}_4\text{-Na}_2\text{SO}_4$ melts and other sulfate mixes such as $\text{MgSO}_4\text{-Na}_2\text{SO}_4$ or $\text{ZnSO}_4\text{-Na}_2\text{SO}_4$ which are also molten at 1300°F. An establishment of whether or not cobalt or other metals have unusual electrochemical reactivity in molten salts would be welcome. Another theory proposes that the cathodic reaction, which may occur either at the metal/salt or salt/gas interface for the case of thin molten films on metals, will tend to increase the O^{2-} concentration at that site through the reaction



and produce an alkalinity gradient which can promote dissolution and transport of the different metal oxides (67). Studies such as this which link electrochemical and chemical reaction may prove especially useful for better understanding corrosion in molten salts.

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CORROSION STANDARDIZATION AND STANDARDS

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ABSTRACT

In the United States, there are over 400 standards-writing organizations covering a wide range of applications such as units of measure, terminology, products, processes, performance characteristics, safety, etc. Standardization is defined as the process of formulating and applying rules for an orderly approach to a specific activity for the benefit and with the cooperation of all concerned. A standard is the result of a particular standardization effort, approved by a recognized body, and takes the form of a document containing a set of conditions to be fulfilled or an object for comparison. This paper reviews the corrosion standardization activity in the United States, lists corrosion standards, and uses a case study to demonstrate the corrosion standardization procedure.

INTRODUCTION

In the United States, there are over 400 standards-writing organizations covering a wide range of applications such as units of measure, terminology, products, processes, performance characteristics, safety, etc. Standardization is defined as the process of formulating and applying rules for an orderly approach to a specific activity for the benefit and with the cooperation of all concerned. A standard is the result of a particular standardization effort, approved by a recognized body, and takes the form of a document containing a set of conditions to be fulfilled or an object for comparison. Five kinds of standards are developed within the standards-writing community: company standards, industry standards, professional standards, government standards and full consensus standards. The principle difference between these kinds of standards is the degree of consensus achieved. Voluntary consensus standards are those developed through the voluntary participation of all interested parties and just as they are developed voluntarily, they are also used voluntarily. Mandatory standards are those developed by a government agency or those from a voluntary system which are referenced by a government agency. The two major organizations in the United States involved with corrosion standardization are the American Society for Testing and Materials Committee G-1 on Corrosion of Metals

and the National Association of Corrosion Engineers. Other organizations may have some corrosion standardization activity but only as a part of a broader standard. This paper reviews the corrosion standardization activity in the United States, lists corrosion standards, and uses a case study to demonstrate the corrosion standardization procedure.

TYPE OF STANDARDS

Five kinds of standards are developed within the standards-writing community. The major difference being the degree of consensus achieved in the standards-development process.

A. Company Standard - This type of standard is the result of consensus among employees of a given organization. An automobile manufacturer has devised a corrosion test for stainless steel trim material. This drip and dry test is therefore used as an indication of the durability of this material.

B. Industry Standard - This type of standard results from consensus among companies within a given industry. Usually, a trade association is involved in the development of this type of standard. The Aluminum Association has developed corrosion standards for aluminum and aluminum alloys which are adhered to by the aluminum producers.

C. Professional Standard - This type of standard results by consensus among individual members of a professional society. For example, the Society of Automotive Engineers has developed specifications for many years. The standard SAE J1047 entitled "Tubing-Motor Vehicle Brake System Hydraulic" includes corrosion test procedures and minimum requirements for this tubing in salt spray and cyclic humidity tests.

D. Government Standard - Consensus is achieved among employees of a government agency or department. For example, a metal part, purchased by a school district, town or city, state, or federal government, would have to meet certain corrosion resistance requirements.

E. Full Consensus Standards - This type of standard has consensus among all that have an interest in the development and/or use of the standard. These include producers, users, and those representing the general interest group.

BENEFITS OF COMMERCIAL STANDARDIZATION

Standards greatly simplify commerce in a highly industrialized society such as ours. As pointed out earlier, their absence would greatly complicate the task of the user in specifying his needs and of the producer in meeting them. Standards provide:

- Improved communication between buyer and seller.
- Greater user confidence in the commodities he buys.
- Better understanding of how to use the commodity.
- Greater public safety in the use of the commodity.
- Better quality control.
- Lower inventories for both producer and user through elimination of unnecessary grades.
- Earlier delivery because of the ability to stock standard items.
- Better performance at lower prices through reduced need for negotiations and more efficient inspection and testing.
- Lower prices to the user through more rational basis for competitive bidding.

VOLUNTARY CONSENSUS STANDARDS AND MANDATORY STANDARDS

Voluntary consensus standards are those developed through the voluntary participation of all interested parties. Producers, users, ultimate consumers, and representatives of government and academia all may have a voice in the development of these standards. And just as they are developed voluntarily, they are also used voluntarily. Their use becomes mandatory only when they are referenced by a government regulatory agency. Building codes, for example, reference hundreds of standards, ASTM and other. Since building codes are the province of government, the referenced standards have the force of law and must be adhered to.

Mandatory standards are those developed by a government agency or, as stated above, those from the voluntary system which are referenced by a government agency -- state, local, or national.

One example of a voluntary consensus standard being used as a mandatory standard is the reference by government agencies of ASTM B117, "Salt Spray (Fog) Testing" (for example MIL-STD-202 Method 101). This ASTM standard is the most widely used corrosion standard in the United States.

The National Association of Corrosion Engineers (NACE) has developed standards relating to cathodic protection of pipeline. These standards result from a combined effort of all interested parties. The technological task was that of developing reliable, reproducible standard methods for implementing cathodic protection of pipelines.

The Department of Transportation has provided a mandatory regulation on cathodic protection of gas pipelines consisting of the following three parts: (1) new construction, (2) existing pipelines, (3) monitoring of corrosion control and record keeping. In developing these minimum requirements for corrosion control, use was made of the National Association of Corrosion Engineers Standard RP-01-69 "Recommended Practice-Control of External Corrosion on Underground or Submerged Metallic Piping Systems."

CORROSION STANDARDIZATION

Out of the 400 standards-writing organizations, only two are totally involved with writing corrosion standards: American Society for Testing and Materials Committee G-1 (ASTM G-1) and National Association of Corrosion Engineers (NACE).

ASTM COMMITTEE G-1

In 1963 the ASTM Board of Directors authorized the appointment of an ad hoc committee on deterioration of materials, including the corrosion of metals. The recommendations of this committee resulted in the formation of the G-group of committees in January 1964. G-1 was designated as the coordinating committee responsible for corrosion activities in ASTM. Committee B-3 on Corrosion of Nonferrous Metals and Alloys was dissolved and its active programs were assimilated by appropriate subcommittees in G-1.

The object of the establishment of Committee G-1 was to centralize all ASTM corrosion work in one technical committee. At the same time it was realized that existing test programs underway in other committees might best be completed in those committees. In some cases, as in the B-3 programs, entire subcommittees and their programs were transferred intact to G-1.

The scope of Committee G-1 is the promotion and stimulation of research, the collection of engineering data, and the development of methods of test, recommended practices, definitions, and nomenclature relating to the corrosion of metals.

Committee G-1 has over 350 members and has two formal meetings each year. The Committee consists of 8 Standing Committees of the Executive Board and 12 Subcommittees (See Appendix A for listing).

ASTM STANDARDS DEVELOPMENT PROCEDURE

When a task group or section produces a draft document, it is reviewed by its parent subcommittee through a balloting procedure. If it is approved by 2/3 of those returning

ballots (a minimum of 60% of the voting interests must return ballots), the document proceeds to a main committee ballot. Here, 90% of those returning ballots (again, a 60% return is required) must approve the document. It then goes to Society ballot, which means that each of ASTM's members has an opportunity to comment on it. Of those who comment (a minimum of 50 ballots is required), 90% must vote affirmatively.

All negative ballots must be considered by the originating subcommittee before a document can be published as a standard. To be valid, a negative must be accompanied by a written explanation of what the writer deems improper technical or procedural considerations. The negative is then judged persuasive or non-persuasive, and the writer is so advised. If it is judged persuasive, the document is rewritten to incorporate the writer's comments. If it is judged non-persuasive, the document proceeds to the next balloting level. This procedure applies at all balloting levels ... subcommittee, main committee, Society.

Once the document has received Society approval, it is submitted to ASTM's Committee on Standards for procedural, rather than technical, review. Following approval by the Committee on Standards, the document is published as an official ASTM standard. Periodically, it is rereviewed and reballoted.

With the approval of the originating committee, the standard is then submitted to the American National Standards Institute (ANSI) for acceptance as an American National Standard. Ultimately, the standard may become a candidate for acceptance and use as an international standard.

The schedule of events, in Table I, for approval of G-61, "Recommended Practice for Conducting Cyclic Potentiodynamic Polarization Measurements for Localized Corrosion," can be used as an example of the ASTM standards development procedure. Committee G-1 established the need for such a standard in late 1973. The finished standard was approved by the ASTM Committee on Standards in early 1979. Over five years time elapsed during the development of this difficult and important standard.

A list of corrosion standards under the jurisdiction of ASTM Committee G-1 appears in Appendix B. In addition, other corrosion related standards exist under the jurisdiction of other ASTM Committees. These are listed in the ASTM Book of Standards Index.

NATIONAL ASSOCIATION OF CORROSION ENGINEERS

The NACE is a technical association concerned exclusively with the protection and performance of materials in corrosive environments. It was organized in 1943 and includes a wide cross-section of industry including metals, refining, petroleum, chemical

processing, plastics, marine environments, pipelines and utilities. The technical arm of the Association is the Technical Practices Committee. The NACE Technical Practices Committee is divided into Group Committees, each devoted to the study of corrosion-related problems in specific industrial disciplines. Each Group Committee is further divided into Unit Committee and Task Groups. One end product of this activity is the publication of standards to provide guidelines for the industrial community.

NACE STANDARDS DEVELOPMENT PROCEDURE

NACE standards are prepared and issued by the NACE Technical Committees. These standards serve as guidelines on specific subjects in the field of corrosion prevention and control. The actual preparation and writing of a NACE standard is the responsibility of a Task Group.

When a NACE Unit Committee Chairman determines the need for the development of a standard, a Task Group is formed with the approval of the NACE Group Chairman. When the Task Group has reached agreement on the text of a proposed standard, the draft is edited by NACE Headquarters. It is then reviewed by the Unit Committee Chairman and subsequently by the NACE Technical Practices Committee, the TPC Reference Publications Committee and the Group Committee. After review, it is discussed at meetings of the Unit Committee. When accepted, the proposed standard is submitted to the Group Chairman for Group Committee balloting. Group Committee approval of a proposed NACE standard is obtained by letter ballot of the Group members. A return of a minimum of 2/3 of the ballots is required. Approval requires that 90% of the ballots returned be affirmative, excluding those ballots marked "not voting". (three types of votes include negative, affirmative, and not voting) Negative votes are resolved or a letter ballot is sent to all Group members to override a negative vote. A 75% affirmative vote is required excluding the ballots marked "not voting." The document is then submitted to the Technical Practices Committee Chairman for approval and then forwarded to the NACE Board of Directors for ratification. This ratification requires an affirmative response from 2/3 of the voting members. NACE standards are reviewed periodically and reapproved or withdrawn.

A list of NACE corrosion standards appears in Appendix C.

METAL STANDARDIZATION

There are about a dozen nationally recognized organizations which develop metals-related specifications. However, four organizations are responsible for 95% of all metals specifications: (1) ASTM, (2) AMS, (3) and (4) Federal and Military specifications. In many cases these specifications are corrosion

related. It is difficult to collect all of the pertinent standards but a collection of key indexes is quite valuable. The most important in the metals field are:

- a) ASTM Index to Standards
- b) AMS Index to Specifications
- c) Federal Index to Standards and Specifications
- d) DOD Index to Standards and Specifications
- e) Index to Chemically Similar Metals and Alloys - MIL-HDBK-H1D
- f) U.S. Voluntary Engineering Standards (NBS Publication No. 329)
- g) Index of Metals Abstracts -ASM

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TABLE I

Schedule of events for approval of G-61, Recommended Practice For Conducting Cyclic Potentiodynamic Polarization Measurements For Localized Corrosion.

<u>EVENT</u>	<u>DATE</u>
1) Task Group on electrochemical tests for pitting and crevice corrosion established.	Nov., 1973
2) Alloys accumulated for round robin tests.	Dec., 1973
3) Test procedure established and round robin materials distributed.	March, 1974
4) Round robin tests completed.	May, 1974
5) Test results discussed at Task Group meeting.	Nov., 1974
6) Subcommittee approved preparation of a Recommended Practice.	June, 1975
7) First draft prepared and circulated for Task Group comments.	Nov., 1975
8) First draft sent out for subcommittee ballot.	Nov., 1976
9) Draft revised and reballoted in subcommittee.	May, 1977
10) Third draft prepared and balloted at main and subcommittee level, submitted to committee on editorial review.	Nov., 1977
11) Negatives on main committee ballot resolved and submitted for society ballot.	May, 1978
12) Placed on society ballot.	Oct., 1978
13) Approved by committee on standards.	Jan., 1979
14) Published in Book of Standards.	Oct., 1979

APPENDIX A

ASTM COMMITTEE G1 ON CORROSION OF METALS

STANDING COMMITTEES

G01.91	Editorial Review
G01.92	Statistical Analysis and Planning of Corrosion Testing
G01.93	Long Range Planning
G01.94	Standard Reference Materials
G01.95	Technical Advisory Group for ISO/TC 156 on Corrosion of Metals.
G01.96	Awards
G01.97	Publicity
G01.98	Advisory on Exposure Test Facilities
G01.99	Liaison

SUBCOMMITTEES

G01.02	Nomenclature
G01.04	Atmospheric Corrosion
G01.05	Laboratory Corrosion Tests
G01.06	Stress Corrosion Cracking and Corrosion Fatigue
G01.07	Galvanic Corrosion
G01.08	Corrosion of Nuclear Materials
G01.09	Corrosion in Natural Waters
G01.10	Corrosion in Soils
G01.11	Electrochemical Measurements in Corrosion Testing
G01.12	In-plant Corrosion Tests
G01.13	High Temperature Oxidation and Corrosion by Gases
G01.14	Corrosion of Reinforcing Steel

APPENDIX B

ASTM STANDARDS

B 117	Salt Spray (Fog) Testing
B 287	Acetic Acid-Salt Spray (Fog) Testing
G 1	Recommended Practice for Preparing, Cleaning, and Evaluating Corrosion Test Specimens.
G 2	Recommended Practice for Aqueous Corrosion Testing of Samples of Zirconium and Zirconium Alloys.
G 3	Recommended Practice for Conventions Applicable to Electrochemical Measurements in Corrosion Testing.
G 4	Recommended Practice for Conducting Plant Corrosion Tests.
G 5	Recommended Practice for Standard Reference Method for Making Potentiostatic and Potentiodynamic Anodic Polarization Measurements.
G 15	Definition of Terms Relating to Corrosion and Corrosion Testing
G 16	Recommended Practice for Applying Statistics to Analysis of Corrosion Data.
G 28	Detecting Susceptibility to Intergranular Attack in Wrought Nickel-Rich, Chromium-Bearing Alloys.
G 30	Recommended Practice for Making and Using U-Bend Stress Corrosion Test Specimens.
G 31	Recommended Practice for Laboratory Immersion Corrosion Testing of Metals.
G 32	Vibratory Cavitation Erosion Test
G 33	Recommended Practice for Recording Data from Atmospheric Corrosion Tests of Metallic-Coated Steel Specimens.
G 34	Test for Exfoliation Corrosion Susceptibility in 7XXX Series Copper-Containing Aluminum Alloys (EXCO Test).
G 35	Recommended Practice for Determining the Susceptibility of Stainless Steels and Related Nickel-Chromium-Iron Alloys to Stress Corrosion Cracking in Polythionic Acids.
G 36	Recommended Practice for Performing Stress Corrosion Cracking Tests in a Boiling Magnesium Chloride Solution.
G 37	Recommended Practice for Use of Mattsson's Solution of pH 7.2 to Evaluate the Stress-Corrosion Cracking Susceptibility of Copper-Zinc Alloys.
G 38	Recommended Practices for Making and Using the C-Ring Stress-Corrosion Cracking Test Specimen.
G 39	Preparation and Use of Bent-Beam Stress-Corrosion Specimens.
G 40	Definition of Terms Relating to Erosion by Cavitation and Impingement
G 41	Recommended Practice for Determining Cracking Susceptibility of Titanium Alloys Exposed Under Stress to a Hot Salt Environment.
G 43	Acidified Synthetic Sea Water (Fog) Testing
G 44	Recommended Practice for Alternate Immersion Stress Corrosion Testing in 3.5% Sodium Chloride Solution.
G 46	Recommended Practice for Examination and Evaluation of Pitting Corrosion.
G 47	Recommended Practice for Determining Susceptibility to Stress Corrosion Cracking of High-Strength 7XXX Aluminum Alloy Products.
G 48	Test Methods for Pitting and Crevice Corrosion Resistance of Stainless Steels and Related Alloys by the Use of Ferric Chloride Solution.
G 49	Recommended Practice for Preparation and Use of Direct Tension Stress Corrosion Test Specimens.
G 50	Recommended Practice for Conducting Atmospheric Corrosion Tests on Metals.
G 51	Test Method for pH of Soil for Use in Corrosion Testing.
G 52	Recommended Practice for Conducting Surface Seawater Exposure Tests of Metals and Alloys.
G 54	Recommended Practice for Simple Static Oxidation Testing.
G 57	Method for Field Measurement of Soil Resistivity Using the Wenner Four-Electrode Method.
G 59	Practice of Conducting Potentiodynamic Polarization Resistance Measurements.
G 60	Practice for Conducting Cyclic Humidity Tests.
G 61	Practice for Conducting Cyclic Potentiodynamic Polarization Measurements for Localized Corrosion.

APPENDIX C

NACE STANDARDS

RECOMMENDED PRACTICES

- RP-01-69 Control of External Corrosion on Underground or Submerged Metallic Piping Systems.
RP-01-70 Protection of Austenitic Stainless Steel in Refineries Against Stress Corrosion Cracking by Use of Neutralizing Solutions During Shut Down.
RP-01-72 Surface Preparation of Steel and Other Hard Materials by Water Blasting Prior to Coating or Recoating.
RP-02-72 Direct Calculation of Economic Appraisals of Corrosion Control Measures.
RP-03-72 Method for Lining Lease Production Tanks with Coal Tar Epoxy.
RP-04-72 Methods and Controls to Prevent In-Service Cracking of Carbon Steel (P-1) Welds in Corrosive Petroleum Refining Environments.
RP-05-72 Design, Installation, Operation, and Maintenance of Impressed Current Deep Groundbeds.
RP-01-73 Collection and Identification of Corrosion Products.
RP-02-73 Handling and Proper Usage of Inhibited Oilfield Acids.
RP-01-74 Corrosion Control of Electric Underground Residential Distribution Systems.
RP-02-74 High Voltage Electrical Inspection of Pipeline Coatings Prior to Installation.
RP-01-75 Control of Internal Corrosion in Steel Pipelines and Piping Systems.
RP-02-75 Application of Organic Coatings to the External Surface of Steel Pipe for Underground Service.
RP-03-75 Application and Handling of Wax-Type Protective Coatings and Wrapper Systems for Underground Pipelines.
RP-04-75 Selection of Metallic Materials to be Used in all Phases of Water Handling for Injection into Oil Bearing Formations.
RP-05-75 Design, Installation, Operation and Maintenance of Internal Cathodic Protection Systems in Oil Treating Vessels.
RP-06-75 Corrosion Control of Offshore Steel Pipelines.
RP-07-75 Preparation and Installation of Corrosion Coupons and Interpretation of Test Data in Oil Production Practice.

RP-01-76 Control of Corrosion on Steel, Fixed Offshore Platforms Associated with Petroleum Production.
RP-02-76 Extruded Asphalt Mastic Type Protective Coatings for Underground Pipelines.
RP-03-76 Monolithic Organic Corrosion Resistant Floor Surfacing.
RP-01-77 Mitigation of Alternating Current and Lightning Effects on Metallic Structures and Corrosion Control Systems.
RP-01-78 Design, Fabrication, and Surface Finish of Metal Tanks and Vessels to be Lined for Chemical Immersion Service.
RP-02-78 Design and Operation of Stripping Columns for Removal of Oxygen From Water.

TEST METHODS

- TM-01-69 Laboratory Corrosion Testing of Metals for the Process Industries.
TM-01-70 Visual Standard for Surface of New Steel Airblast Cleaned with Sand Abrasive.
TM-02-70 Method of Conducting Controlled Velocity Laboratory Corrosion Tests.
TM-01-71 Autoclave Corrosion Testing of Metals in High Temperature Water.
TM-01-72 Antirust Properties of Petroleum Products Pipeline Cargoes.
TM-01-73 Methods for Determining Water Quality for Subsurface Injection Using Membrane Filters.
TM-01-74 Laboratory Methods for the Evaluation of Protective Coatings Used as Lining Materials in Immersion Service.
TM-02-74 Dynamic Corrosion Testing of Metals in High Temperature Water.
TM-03-74 Laboratory Screening Tests to Determine the Ability of Scale Inhibitors to Prevent the Precipitation of Calcium Sulfate and Calcium Carbonate from Solution.
TM-01-75 Visual Standard for Surfaces of New Steel Centrifugally Blast Cleaned with Steel Grit and Shot.
TM-02-75 Performance Testing of Sucker Rods by the Mixed String, Alternate Rod Method.
TM-03-75 Abrasion Resistance Testing of Thin Film Baked Coatings and Linings Using the Falling Sand Method.
TM-01-77 Testing of Metals for Resistance to Sulfide Stress Cracking at Ambient Temperatures.

APPENDIX C

MATERIAL REQUIREMENTS

- MR-01-74 Recommendations for Selecting Inhibitors for Use as Sucker Rod Thread Lubricants.
- MR-02-74 Material Requirements in Prefabricated Plastic Films for Pipeline Coatings.
- MR-01-75 Materials for Valves for Resistance to Sulfide Stress Cracking in Production
 and Pipeline Service.
- MR-01-76 Metallic Materials for Sucker Rod Pumps for Hydrogen Sulfide Environments.

CORROSION PROTECTION BY COATINGS

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ABSTRACT

The basic research program of the Paint Research Institute on the protection of surfaces by polymer coatings follows four general paths:

1. Barrier properties of the coating.
 2. Interference with the corrosion mechanism.
 3. Assuring adequate bonding of the coating.
 4. Locating the anodic areas in a corroding system.
- These directions were established as the result of an encounter session on corrosion control held between a group of coatings scientists and experts from fields bearing on corrosion. The meeting resulted in the writing of a *research prospectus* upon which academic scientists based proposals for research support. The evolution of the prospectus and directions taken by corrosion research as a result of it are presented.

INTRODUCTION

Research styles have changed drastically over the years. In no technological area is this change more pronounced than in coatings research, where the nature of the research conducted has been altered as drastically as has the lifestyle of the researcher.

Coatings research began when polymers were less respectable than they are now. Naturally-drying oils provided the vehicles, the atmosphere provided the energy to dry them, and earth pigments accounted for most of the hiding. New polymers with tailored functionality were not on the market, and the finishing of manufactured articles was accepted as a time-consuming process. And one never set a drink on the parlor table.

The earliest advances in coatings science came with improved drying through the selection of catalysts, followed by improved mechanical properties through the introduction of resins. Somewhere during this development it became evident that pigments could do more than hide, for some were found to impart corrosion resistance to metallic substrates. All of them contributed to a paint's viscosity, and one of the first useful scientific contributions made exclusively by coatings scientists (the critical pigment volume concept) was discovered as a result of physical chemical studies on pigments.

In the realm of corrosion control, as contrasted with an understanding of the mechanisms of corrosion, research has not been carried out in a concerted fashion. A sizeable percentage of the 72 billion

dollars estimated to be lost annually to corrosion could be prevented with better design and maintenance, including coating. Many basic research accomplishments have been made in the last half century that have enabled coatings to keep pace with other technologies, and at least one significant achievement has been made in corrosion protection by electro-deposited primers (especially cathodic), but advances in this quarter have been rare.

Red lead in linseed oil used to offer fair corrosion protection. Then synthetic resins began to appear and chromates became the protective ingredient, either as a solution pretreatment or as a pigment. Today both lead and chromium are recognized toxins and the coatings industry is caught without a suitable substitute. Basic research must move fast if it is to supply answers to this practical problem, for little is known about the mechanism of corrosion protection.

CORROSION INHIBITION

The effectiveness of a coating ingredient in imparting corrosion resistance may result from at least two separate characteristics: assisting in the formation of a passive film, as most metals do, or adsorbing at the interface in a manner which mimics the formation of reaction products. Corrosion rates are quite slow when the metals are covered by oxide films, and materials such as phosphates and chromates participate in the film-forming process. Adsorption (generally by organic polymer molecules) is not considered as reliable a method of protection.

Inasmuch as the kind of corrosion protection afforded by coatings involves the metal surface, one approach to corrosion inhibition is a study of the electrode potentials of the metal. These potentials represent the solution oxidizing power of the metal, and as one would expect, the corrosion rate increases in direct proportion to this quantity. However, Fontana and Greene showed that a limiting corrosion rate is soon attained and further increases in electrode potential drastically reduce the corrosion rate. The metal enters a passive region and resists corrosion until a further threshold in electrode potential is reached.

An even more basic approach to corrosion inhibition based on thermodynamic arguments has been provided by Kruger. Starting with Pourbaix Diagrams in which potential is plotted as a function of pH he shows that the demarcation between the active region (at low pH for iron) and the passive region depends on the oxygen concentration. As the partial pressure of oxygen in the environment of the metal decreases, the pH for the transition moves from 2 to as high as 7, thereby facilitating the dissolution of iron, rather than retarding it. Further decreases in oxygen concentration lead eventually to complete passivity. Clearly, inhibition involves something more than denial of oxygen, for if the barrier properties of a coating are relied upon to inhibit corrosion a dangerous situation is created if the barrier falls short of perfection (as most do).

Because of the dependence on pH, one role of an inhibitor could be as a buffer. Industrial atmospheres contain acidic components ranging from CO₂ to SO₂, and corrosion is especially severe in those atmospheres. Many inhibitors are believed to adsorb on a metal surface and prevent such attack from taking place.

THE DIRECTION OF COATINGS RESEARCH

In medieval times a scientist such as Leonardo da Vinci (or an explorer like Columbus) had to find a royal patron to finance his investigations. Centuries later the patronage concept was still in evidence: science departments of universities responded to the industrial revolution by allowing faculty released time for research, and the more enterprising among them ultimately found outside support by writing unsolicited research proposals. Prior to 1957, in an effort to steer some of this research our way, various local societies of coatings technologists had begun to support faculty at universities in their geographic area whose research appeared relevant to coatings; and in 1957 this support came under the PRI umbrella.

Early PRI Effort

University projects on dispersion of pigments in media, on chalking of weathered surfaces, and on polymer physical chemistry were brought under the direction of my predecessor, Dr. J. S. Long, and research continued along the lines of interfacial chemistry, rheology, and physical chemistry in general for a decade or more. By 1967 the list of projects was quite varied, covering such topics as paint drying, interactions at various interfaces, photochemical reactions in polymers, mechanical coagulation, diffusion, color, rheology, and solubility.

As company in-house research turned more and more toward analyzing the competitors' polymers and toward less expensive formulations, of which concern for the ecology is a corollary, PRI research got more deeply involved in mechanical properties, adhesion, thermodynamics, and other borderline areas that gave an interdisciplinary flavor to the effort. Yet, something was missing, for the professors' solutions often were found in need of problems rather than the other way around.

In 1971 the PRI Trustees decided in a sweeping change of policy to support *research by prospectus*. Before considering the consequences of that innovation one needs to consider the requirements of a protective coating in order to recognize the interdisciplinary flavor of our task. A coating must, first of all, flow onto and wet the substrate; it must displace species already present on the surface, then continue to adhere and maintain film integrity while developing desired optical properties; and it must continue for a reasonable period afterward to serve as a barrier to moisture and corrodents, thereby resisting the elements that it is helping the substrate to resist. Compare these requirements with the abbreviated list of desiderata for man's earliest recorded use of paint on the cave walls at Lascaux, where the only requirements were permanent hiding and adhesion in an environment that remained benign for millenia until the caves were invaded by tourists.

EVOLUTION OF CORROSION PROSPECTUS

The manner in which a prospectus evolves is of interest, for it elucidates the process whereby a consensus is attainable after only a single day's encounter. The meeting at which the Paint Research Institute Corrosion Encounter (PRICE) was conducted was preceded by a questionnaire to the twelve participants asking what problems need solution by what fundamental approaches involving certain limitations as to the goals. For example, the coatings

scientists on the panel quickly pointed out that a study of corrosion mechanisms was not desired and that protection by coatings was the subject.

The resulting questionnaire which served as the agenda for the morning session is given so that its metamorphosis into a prospectus can be shown:

- "1. What is the most significant scientific problem in corrosion control?
 - a. Knowledge of interface chemistry?
 - b. Knowledge of electrochemistry?
 - c. Identifying reagents, products, inhibiting factors?
 - d. Localized nature of corrosion?
 - e. Mechanism of onset and propagation of corrosion reaction?
 - f. The need for predictive and test methods?
 - g. Other.
2. What fundamental approach will enable coatings to improve the corrosion resistance of metals?
 - a. Delineation of how coatings function?
 - b. Characterization of surfaces, interfaces, and layers?
 - c. Determination of cell parameters?
 - d. Description of corrosion chemistry?
 - e. Other.
3. What factors limit the degree to which coatings can improve corrosion control?
 - a. Transport properties?
 - b. Interfacial properties?
 - c. Chemistry of the substrate?
 - d. Other
4. How does the onset of corrosion differ from its propagation?
 - a. Stress?
 - b. Passivation?
 - c. Domains?
 - d. Is there a message here for termination of corrosion?
 - e. How do coatings influence the course of corrosion?"

The afternoon session began with one of the issues firmly in place and with a more specific questionnaire serving as the discussion agenda:

"Our objective is to write a research prospectus, designed to elicit proposals or to be sent to target individuals.

Evaluation of proposals will be based on their probability of creating knowledge of extending the life of metal structures in corrosive atmospheres.

(It is assumed that transport properties of films involving selected corrodents and charged species will constitute our first proposal.)

1. What is the complete chemical reaction in the chloride-induced corrosion of iron?
2. How are the spacings of the cathodic and anodic areas determined? What is their origin? Do magnetic domains play a role?
3. How does the onset of corrosion differ fundamentally from the propagation of corrosion? What role is played by oxide species in the propagation?
4. How can passivation or inhibition be achieved via layering, utilizing oxide layers, other inorganic species, and organic coatings? How is corrosion terminated, once started?"

The encounter session eventually led to the four general areas for which research support could be justified. These became part of the prospectus published in *J. Coatings Technology* 45 (No. 584), 61-64, (1973):

1. Barrier Properties of Coatings
 - a. *Studies of Free Films* via ionic diffusion rates and perselectivity, by membrane potentials, capacitance, and radiotracers. Parameters to be studied: the anion, pigmentation, and impressed electrical field.
 - b. *Studies of the Effect of the Interface* via diffusion rates, corrosion rates, and peel strength, using water uptake as the parameter.
2. Interference With Chloride-Induced Corrosion Mechanism
 - a. *Literature Analysis*, aiming at the manner in which chlorides attack iron.
 - b. *Monitoring of Ongoing Research* and preparation of synopsis on how basic research answers the question of corrosion stoichiometry.
 - c. *Achievement of Passivation* via identification of the vital factors controlling corrosion. Interference with cations by complexation or reducing species; with anions, by complexation, bridging, or exchange.
3. Bonding of Freshly Exposed Iron to Various Species
 - a. *Creation of Iron-Coating Bond* via exposing nascent iron to species containing various functional groups. Use machining or electro-polishing techniques.
 - b. *Test of Iron-Coating Bonds* via comparison of nascent metal coatings with conventional system.
 - c. *Practical Demonstration* via curing an oligomer attached to a pure metal.
4. Localization of Anodic Areas
 - a. *Scanning Experiments* by a raster method in various environments, and determination of the effect of coating on the scan profile. Relate location of anodic areas to presence of oxide layer.
 - b. *Wandering Phenomenon* via tracing the path of anodic areas in filiform corrosion. Determine how migration can be stopped and explain the difference between the onset of corrosion and its propagation.

RESULTS OF THE PROGRAM

Thirty-nine proposals were received as a result of the prospectus. These were both categorized and rated by a committee comprising four of the twelve experts: Of the eleven top-ranked proposals, three fit into category 1, five into category 2, and three into category 4. Five of these proposals resulted in grants whose results will be discussed as time permits. The most interesting result was achieved in an electrochemical scanning experiment performed by Malcolm Hepworth at the University of Denver, in which a steel cylinder was rotated beneath an electrolyte solution with an electrode scanning device. Localized anodic areas were rendered visible by the potentiometric tracing which resulted. The one grant which covered the barrier properties of coatings (category 1) was based on Lewis acid-base interactions of the pigment and vehicle in several model systems. This interesting concept needs further development along the lines established by Drago wherein acid-base interactions are shown to depend on what portion of the interaction is electrostatic and what portion is covalent.

Studies related to the voltage-current phenomenon described by Fontana and Greene showed that the species involved in the initially active region at low voltage was γ FeOOH. One intermediate in this reaction was postulated to be the species $\text{Fe}(\text{OH})^+$ and this was confirmed in an experiment involving a hemispherical rotating electrode in a solution containing chloride ions. Knowledge of the intermediates is a necessary first step in deciding on a protective measure based on interfering with the corrosion mechanism. In this case it is evident that adsorption by chloride ion is not a factor.

SUBSEQUENT DEVELOPMENTS

Corrosion protection is of such practical significance that strictly fundamental research is not likely to provide immediate answers. It will serve only to guide inventors who continue to use the Edisonian approach, and it will more likely provide the metallurgists and materials engineers with a data base than it will help the coatings formulator.

New methods of characterizing surfaces, such as ESCA, SEM, and other probes offer the coatings scientist many more opportunities to understand and combat corrosion than ever before.

For the long-term approach to corrosion protection there are many fundamental research areas for coatings inhibition, starting with an understanding of why coating sometimes exacerbates localized corrosion. The need for basics that will lead to the discovery of inhibitors is evident, for replacement of chromates is soon to be mandated. Because chromates are virtually unique in displaying both cathodic and anodic inhibition the question revolves around how they reduce electrode efficiency. Do they short out cathodic and anodic regions on the surface, or do they obliterate grain boundaries? One needs to answer how they work on a molecular basis.

Research on the barrier properties of coatings is needed. If one excludes water, or ions, or oxygen he solves the problem of corrosion. Since zero diffusion is impossible one must rely on adhesion to exclude these corrodents from the interface. Therefore, in studying the mode of transport of vapors through a film it is necessary to consider their attachment to cathodic and anodic areas, for no metal surface is homogeneous.

Some research is indicated on the synthesis of polymers that impart corrosion resistance. Anodic/cathodic depolarizers need not be sought only in pigments as replacement for chromates; perhaps a polymeric system can be found that possesses the right coupling of oxidation and reduction tendencies--or the right combination of electrostatic and covalent contributions for adduct formation with oxide surfaces.

STATE OF THE ART USING CATHODIC PROTECTION AS A CORROSION CONTROL TOOL. E. W. DREYMAN, Petro-Chemical Associates, Inc. 4 Taft Road, Totowa, N.J. 07512

The history of Cathodic Protection as it has developed from initial marine use thru recent applications on major structures is discussed. Theory and design considerations, galvanic and impressed current anode materials, hardware, cost effectiveness and innovations in cathodic protection use are covered in detail. Problems associated with implementation of programs calling for Cathodic Protection as well as limitations in its use are also a part of this paper. Developments in Cathodic Protection on a world-wide basis with a comparison of these activities with U.S. efforts is outlined, covering such items as compatibility of coatings and alloy considerations. Finally, a consideration of some future applications of Cathodic Protection of Cathodic Protection are given.

(Text of manuscript was not provided for publication.)

INHIBITORS FOR PREVENTION OF CORROSION

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ABSTRACT

Chemical Inhibitors are added in small concentrations to reduce corrosive liquids' attack on active metals. Their advantages and disadvantages are compared with other methods of corrosion control such as metallurgy, coatings, etc. Although the use of a satisfactory inhibitor system is usually specific to the metal and to the environment, some useful generalizations exist. The fundamental concepts of these are developed from the standpoint of electrochemistry of the system and the nature of the inhibitor molecule(s).

Examples are given of important applications of inhibitors in water-treating for industries in general and in specific industries such as metal working, petroleum production, transportation and refining. The changing requirements for inhibitors effected by recent environmental restrictions are discussed.

FUNDAMENTAL CONCEPTS IN CORROSION INHIBITION AND INHIBITORS

Corrosion inhibition by chemical inhibitors has been under both extensive and intensive investigation for the past fifty years. Useful information has been obtained in basic concepts of inhibitor action, but there are still many gaps in the knowledge and serious controversies concerning the fundamentals. The present discussion will present the viewpoints of this speaker, whose feeling is that the theoretical concepts have limited, but nevertheless useful, applications in the development and application of inhibitors. The practical application of inhibitors is wide-spread in a number of important industries, and some of these will be discussed. Limitations of a complete understanding of inhibitor action do not in general limit their application in many areas where they are economically effective and can supplant and/or supplement other methods of corrosion control such as by metallurgical alterations and by use of protective coatings.

In the following discussion a corrosion inhibitor will be defined as a material which when added in "small" quantities to a corrosive fluid, a liquid or condensed vapor, causes an appreciable reduction in the rate and/or nature of attack on a metal normally corroded by the fluid contacting it.

By a "small" concentration, is meant that the gross properties of the corrosive fluid such as pH, electrical conductivity; concentrations of dissolved gases such as oxygen, carbon dioxide and hydrogen sulfide are not altered sufficiently to

vary the corrosion rate from its value in the absence of the inhibitor. Since other authors sometimes include materials, which do change pH, etc., mention will be made of them before proceeding to discussion of inhibitors as defined above. The use of such materials is of considerable economic value, and their importance should not be discounted. Their action is generally well-understood; however, this is not a developing field as are the true inhibitors as we will consider them.

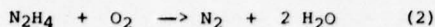
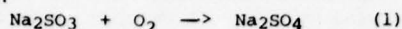
USE OF NEUTRALIZERS, ETC. Iron, steel and other ferrous metals are by far the most important materials used in industry for conservation and processing equipment. They are readily attacked by aqueous solutions of low pH containing mineral acids or other acid-forming materials such as dissolved CO_2 , H_2S , HCN , and low molecular weight organic acids. At pH values below five, depending on the acid constituent, attack is usually too severe to tolerate. An obvious solution is raising the pH by addition of neutralizing alkaline materials such as NaOH , Na_2CO_3 , or Ca(OH)_2 . The use of such inorganic bases is wide-spread in chemical processing and in waste-water treatment and disposal systems. With steel at moderate temperatures, close control of the quantities of neutralizers is not essential except for economic reasons since steel (iron) is not attacked at pH as high as 11-12. At elevated temperatures such as in steam generators, closer pH control is necessary because of the amphoteric nature of iron oxides at elevated temperatures and pH.

Aluminum and zinc (as galvanized steel) are also important materials of construction and are attacked more readily than is steel at low pH values. Additionally, because of the amphoteric nature of their hydroxides, pH values above about nine must be prevented. Ammonia is a material which is used as a neutralizer of acidity, particularly in refinery processing for reacting with HCl and H_2S . These are formed from decomposition of sulfur-bearing organics or from the hydrolysis of calcium and magnesium chlorides contained in the aqueous fluids occluded in the charge stocks to refinery processing units. Ammonia has many practical advantages as a neutralizer compared to the inorganic alkalis previously mentioned. However, a serious disadvantage of ammonia is its attack on copper and copper-bearing alloys at pH values above eight to form soluble cuprammonia coordination compounds.

A small number of organic amines has been developed and used to replace ammonia in refinery and boiler applications for neutralization of acidity. The acid constituent in boiler condensate systems is CO_2 formed by high temperature decomposition of carbonates and bicarbonates in the boiler feed-water. In addition to a number of proprietary formulations, the common amines in use for boiler and process work include cyclohexylamine, morpholine, monoethanolamine, etc. These materials differ from most other similar amines in that their attack on copper and copper-based metals is negligible under the conditions of usage normally employed.

As will be further discussed below, aqueous corrosion of steel at neutral or alkaline pH is accelerated by the presence of dissolved oxygen. For this reason, oxygen is removed by physical and/or chemical methods. Chemical treatment generally employs either (1) sodium sulfite or (2) hydrazine, which react with

oxygen as shown:



Further information on the use of neutralizers and oxygen scavengers is given in the attached references. An important limitation on their use is that stoichiometric quantities of the materials are required so that for treatment of streams of high volume and/or high concentration of corrosive, costs may be so high that other corrosion-preventive methods are economically more attractive.

NON-NEUTRALIZING INHIBITORS In discussing these materials it is useful to consider three criteria all of which are simultaneously necessary for corrosion to occur on a metal. These are:

(1) An active or corrodible metal, such as iron (steel); (2) A corrosive environment, such as a mineral acid; (3) Contact of the metal by its environment.

This concept suggests at least three possibilities for controlling the overall corrosion reaction. We might change the metal's innate properties as by using stainless steel or a noble metal such as silver or gold to replace the active metal. Additionally, by alteration of alloying elements, heat treatments, etc., a metal which is ordinarily too active for use in a given corrosive environment may be rendered sufficiently inactive to give satisfactory performance for the use intended. An example is addition of small amounts of copper and other elements to ordinary carbon steel; this gives the steel sufficient resistance to atmospheric corrosion that only minimum maintenance and protection are required. The field of metallurgy is very important in its relation to corrosion prevention, but it will not be discussed in any detail herein. For extremes of temperature, pressure and chemical reactivity, the metallurgical approach may be the only satisfactory one. Generally, highly resistant materials are very expensive in capital expenditure and sometimes require alloying elements in short supply.

A second approach to reducing the corrosion is by alteration of the corrosive environment. For example, if the corrosivity is caused by low pH, raise the pH. Some of the technology involved in this concept and its limitations were discussed above.

A third possibility is to prevent direct contact between the metal being attacked and the environment which is attacking it. This concept involves the whole field of protective coatings, linings, claddings, etc., which have a very important role in corrosion control. This is a field in itself and will not be covered here in any depth. Use of organic coatings and linings is generally restricted in temperature and pressure as compared to metallurgical methods of corrosion control; however, costs can be much less. An important limitation of protective coatings is the difficulty in industrial work of applying a perfect coating free of pin-holes or other defects. These defects are usually weak spots which allow attack from the solution onto the metal in the vicinity of the weak spots. Not only is this metal subject to the normal attack of unprotected metal, attack may be accelerated since these unprotected areas must bear the full brunt of reaction with the corrosives which could distribute their attack on the entire surface more or less uniformly if the metal were not coated.

Proper quality control and inspection methods can obviate many of the problems of application; however, service damage to the coating may still

allow for attack on the structure to be protected. If such damage can be detected and remedied, the continued value of the coating may be assured. Such is the case for external coatings of structures and equipment. However, detection and repair of coatings on the inside of vessels and in other sites of poor accessibility seriously limit the use of coatings. An ideal situation would be one in which the coating had the ability to repair itself. We will develop this concept below when inhibitors are discussed in detail.

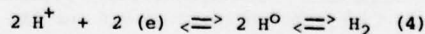
Keeping in mind the three criteria for corrosion as developed above, we see that there are three methods of controlling corrosion as well as the possibility of a number of combinations of two or three of the methods mentioned singly. We will not discuss such combination methods. This is not to discount their value; often a combination offers technical and economic advantages over a single approach.

How should the non-neutralizing inhibitors be classified on the above basis? It is useful to consider that these effectively act in two ways - to change the reactivity of the metal and/or to place a protective barrier between the metal and attacking environment. The electrochemical theory of corrosion, which will be developed in detail in the presentation on Cathodic Protection at this seminar, is most useful in understanding corrosion and its inhibition. Referring to a table of electromotive force for metals in contact with their ions, using hydrogen as a base point or standard, metals are grouped according to their reactivity with hydrogen (i.e., attack by acids) or ability to replace hydrogen from its salts. Those more active than hydrogen are never found free in nature and are called "active" metals. Those less active than hydrogen, which hydrogen replaces from its salts, may be found free in nature and are called inactive (or "noble" if usually found free in nature) and generally are of low activity. Corrosion reactions in aqueous conducting solutions entail two or more reactions or half-cells occurring simultaneously. In acid or neutral solutions, one half cell is the anodic reaction as represented by Equation (3).

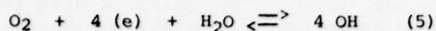


M is generally a reactive metal such as Fe, Al, Zn, Pb, which dissolves to form soluble ions of Fe^{++} , Al^{+++} , Zn^{++} , or Pb^{++} . Note that at the anode metal is lost from the structure and enters into solution.

There must be simultaneous reaction to remove the electrons liberated in (3). Such a reaction occurs at the cathode of the system. The cathode may be another metal electrically connected to the anode, an area of the same metal as the anode but of different electrochemical activity, or some reducible ionic or non-ionic species in the solution in contact with the metal. If the solution is highly acid (low pH), it will have an appreciable concentration of hydrogen ions, H^+ , which will react with the electrons to form atomic and then molecular hydrogen as in Eqn. (4)



In neutral or alkaline solutions, reaction (4) is very slow, and another cathodic reaction such as (5) will occur if the system contains dissolved oxygen;



Note that there is no metal loss at the cathodes of either (4) or (5); that hydrogen gas is evolved in (4). In (5), there is no gas evolution, but hydroxide ions are formed, so that the pH in the vicinity of the cathode will rise.

Since the overall production and consumption of electrons in the system must balance, the net anodic and cathodic reactions must be equal and can be represented by simple stoichiometric and electrochemical relations. This does not mean that the intrinsic rates of the individual reactions are the same; in fact, they usually differ widely. The net or overall corrosion reaction is mainly dependent on the slowest reaction. If this is the cathodic reaction(s), the system is said to be under cathodic control; if the anodic reaction is the slowest, it is under anodic control; if the anodic and cathodic reactions are roughly of equal velocity, the system is said to be under mixed control.

Treatment of a system with inhibitors involves adding something which alters the anodic reaction (anodic inhibitor), the cathodic reaction(s) - (cathodic inhibitor), or both reactions (mixed inhibitor).

Using the analogy of the chain and its weakest link, it would be desirable to inhibit the reaction which is the slowest and therefore, controlling. In most industrial systems such as active metals in acids and in cooling and boiler water, this is the cathodic reaction. A common cathodic inhibitor in cooling water systems is soluble zinc ion, the action of which can be understood from equation (5). At the cathode, either gross or local, pH rises because of the production of hydroxide to give the relatively insoluble zinc hydroxide. This acts as a barrier to further diffusion of oxygen to the metal surface and thus slows the cathode reaction and the overall corrosion rate. Another common cathodic inhibitor is calcium ion, which in hard waters under the proper conditions, forms insoluble $CaCO_3$ at the cathode(s). Certain natural products such as gelatin at one time were also used as cathodic inhibitors in acid pickling of metals. Unfortunately, cathodic inhibitors used by themselves require high concentrations of additives and are not usually cost-effective.

Anodic inhibitors are more common and are generally used in small dosages, measured in parts per million of the liquid to which they are added. The oldest, most widely used and most cost-effective material is chromate ion, CrO_4^{2-} , added as sodium chromate or bichromate or other soluble salt.

Although there have been many studies of its action during the past sixty years, the action of chromate on steel and other metals is not entirely understood. It is generally accepted that it oxidizes the anodic areas of the metal, e.g., steel, to form a very tight, adherent, non-reactive oxide which acts as a molecular barrier to attack by the corrosive solution. The action is similar to that of a protective coating. This oxide differs from that normally formed by the rusting of steel, which is porous and non-protective. Rather is the oxide similar to that on aluminum and on stainless steel and titanium. Both aluminum and titanium are normally very anodic in the e.m.f. series and thermodynamically unstable in the water/air system; however, they are usually attacked but slightly in such systems.

Stainless steels contain nickel and chromium, and when of the proper composition, form mixed oxides

of iron, nickel and chromium, which act as a corrosion barrier. If there is an adequate supply of oxygen in the systems, the normally anodic surface of stainless steel becomes cathodic and is said to be "passivated". Similarly, the action of anodic inhibitors such as chromate is to passivate the surface of ordinary steel when applied under the proper conditions. Although, chromium has been found to be present in the passive film formed on protected steel, its presence cannot be the whole story, since many other oxidizing inorganic ions are also effective passivators.

Despite the technologic and economic advantages of chromate, it has several serious drawbacks. One, which has become increasingly important during the past few years, is the alleged toxicity of the hexavalent Cr to marine and other life which could be affected by the discharge of effluents from systems using it in cooling water and other systems. At this point it should be mentioned that a successful inhibitor application always requires that a certain minimum concentration of treating chemical be present. The reason for this is believed to be that there is a dynamic equilibrium between the surface of the metal and the solution contacting it, and that the protective film is continually broken down and reformed by action of the chemical, such as chromate on the metal. In this respect, we have a self-healing protective coating, which was mentioned above as being desirable from the standpoint of coatings. Since the treatment costs, as well as the environmental hazard, from the treatment are proportional to its concentration, it would be desirable to reduce the concentration as low as possible.

However, there are serious restrictions to reducing an anodic inhibitor such as chromate below recommended levels. The reason is that some areas, protected at high inhibitor concentration, will be unprotected at lowered concentrations, and these areas will suffer localized, increased attack commonly observed as pitting. This is because the overall reaction rate, as stated above, is controlled by the cathodic reactions, the rates of which are practically unaffected by the addition of an anodic inhibitor. If the total number of anodes is reduced by, say 90%, the remaining unprotected 10% now bear the full amount of metal loss, which is hardly changed. Thus, the individual attacked areas will have more metal removed, and the situation may be worse than if no inhibitor at all were used and uniform corrosion occurred over all of the anodic area. For this reason, anodic inhibitors used in systems under cathodic control are called "dangerous inhibitors". Since such are the normal systems and inhibitors in industrial applications, we have a classic illustration of "Murphy's Law"!

Some years ago it was found that use of chromate in conjunction with certain phosphates could give a synergistic effect resulting in less pitting and reduced overall cost of inhibitors. A further development resulted in the use of zinc in combination with chromate and/or phosphate. This is a mixed inhibitor system since the cathodic inhibitor, zinc, reduces the overall corrosion rate through its action on the local cathodes and is not dangerous.

The use of these systems requires close limits of concentrations, pH, types of metals

and other operating parameters controllable in industrial operations, and is extensively described in the corrosion literature. Since phosphates and zinc are also limited in plant effluents, considerable efforts are being made by the vendors and formulators of these systems to develop treatments which are effective, economical in use, non-toxic, etc. This is a very active field of work both from the theoretical and practical standpoint.

Molybdate has been proposed as a material of similar passivating properties to chromate. It has less toxicity but higher application costs, and to date has not found wide acceptance. Nitrites, phosphonates and phosphate esters, silicates and borates are other passivating inhibitors which are used to a limited, although increasing extent, in the place of chromate and are described in the corrosion literature.

ORGANIC ADSORPTION-TYPE INHIBITORS These materials are also known as surfactant or reverse-wetting inhibitors and have wide application in a number of industries such as in the acid-pickling of steel; in petroleum production, transportation and refining; in chemical and petrochemical processing; and in the steel and pulp and paper industries.

They were first developed and investigated in conjunction with acid pickling of steel. The aim of the pickling process is to remove mill-scale from the metal without an undue loss of clean, base metal. Pickling solutions are generally fairly concentrated solutions of strong acids such as sulfuric at temperatures of around 60°C. These are very severe conditions for carbon steel even with short contact times. In addition to the removal of metal, there is also a possibility of embrittlement of the steel caused by the entrance of atomic and/or molecular hydrogen into the metal, and inhibitors are used to minimize both problems.

Inhibitors are added to the pickling baths in fairly high concentrations, of the order of 0.01-1%. The literature on organic inhibitors for this application is voluminous with practically every type of conceivable organic molecule having been investigated and patented. A number of studies have been made on the effect of structure of the inhibitor molecule on its efficiency, and these will be summarized briefly.

Materials investigated include amines (primary, secondary, tertiary, quaternary) - aliphatic, aromatic, heterocyclic; oxygen compounds - ethers, aldehydes, ketones, fatty acids, fatty esters; sulfur compounds - mercaptans, sulfides, disulfides, heterocyclics, thioureas; fatty amine-fatty acid complexes. Molecular structure has included effect of molecular weight and chain branching. The generally accepted explanation of the action of the materials is that they function by adsorption of a single monolayer or, at most, a few monolayers onto the metal normally attacked. The inhibitor molecule contains a polar group such as nitrogen, oxygen and/or sulfur which has a pair of unshared electrons in its outer ring. These are believed to be attracted to areas of electron deficiency on the metal surface resulting in adsorption of the inhibitor molecule through the polar group onto the surface.

This adsorption has an energy of several kilocalories per mole and thus is intermediate between chemical heats of reaction and physical heats of condensation. Plots of amount of material adsorbed per unit surface of metal, obtained by radiotracers and other techniques, generally show a dependency on concentration which is fairly well represented by the simple Langmuir Equation

$$x/a = kc / (1 + kc) \quad (6)$$

where x/a is the amount in moles adsorbed per unit area, c is inhibitor concentration at equilibrium and k is a dimensionless constant characteristic of the inhibitor molecule. If metal, such as finely divided iron powder, which has been equilibrated with a given concentration of inhibitor is placed into inhibitor-free solvent, a considerable portion of the inhibitor is desorbed. It is believed that the amount which is not desorbed is the principal contributor to the inhibitor efficiency and that it forms a mechanical barrier to corrosive reactions occurring on the metal surface. Early investigators believed that the barrier is principally to the cathodic discharge of hydrogen, but later work indicated that adsorption occurs on anodic areas as well, so that it is probably satisfactory to assume general adsorption. In a homologous series of materials, e.g., aliphatic amines, the value of k in equation (6) increases with molecular weight according to Traube's Rule of Adsorption. Thus the amount of inhibitor required for a given amount of adsorption, or for effecting a given amount of corrosion reduction (which appears to be proportional to this adsorption) falls off as the homologous series is ascended. The present author has found that an increase of four carbon atoms in the chain length effects an increase of one order of magnitude in the Langmuir constant. Up to about 16-18 carbon atoms, efficiency increases with chain length. Above this, there is little change, possibly because the higher molecular weight materials have such limited solubility that there is insufficient concentration in solution to be more effective than the C-16 to C-18 homologs.

The ease of adsorption and difficulty of desorption complement each other, and increasing the number or strength of the polar groups usually increases adsorption and makes for better inhibition. Thus the aliphatic amines, which are stronger bases than the aromatic amines, are also better inhibitors.

The strength of adsorption between the inhibitor and the metal may be greatly enhanced if there is specific interaction between the two as when a coordination or chelant complex is easily formed. Thus, a number of heterocyclic sulfur and nitrogen compounds such as mercaptobenzo thiazole, benzotriazole, and their derivatives react strongly with copper to give insoluble films on the metal which prevent tarnishing, etc. In cooling water systems, small amounts of these additives in the inhibitor formulation prevent the corrosion of the copper-based components of the processing system. Corrosion on these is not normally objectionable, per se; however, the small amounts of soluble ions which get into the system may plate out on the steel components to form metallic copper and set up corrosion cells. Here copper is cathodic to the steel, which suffers accelerated pitting.

Other chelating molecules such as 8-hydroxy quinoline on aluminum and ethylene diamine tetra-acetic acid might be appreciable for aluminum and steel respectively if proper solubility and other considerations are controlled.

The function of the non-polar hydrocarbon radical on the inhibitor molecule is to form a water-repellant film oriented nearly perpendicular to the metal surface to act as a barrier to ingress/egress of corrosives and corrosion products onto/from the metal surface. Scaled molecular molecules show that branching of the chains is detrimental in forming a tight

monolayer, and generally branched chained molecules are somewhat less effective inhibitors than straight chain isomers of the same molecular weight.

INHIBITORS IN THE PETROLEUM INDUSTRY Extensive use is made of corrosion inhibitors in petroleum production and refining and to a lesser extent in the transportation of crude stocks and finished products. This usage is described extensively in the trade and patent literature and references are given at the end of this paper. The general action of inhibitors is that of forming an oriented adsorbed film with the hydrocarbon tail of the inhibitor molecule acting as a water-repellant protective barrier against aqueous fluids which would normally attack the metal, thus the terminology "reverse-wetting inhibitors". Production of petroleum, natural gas and gas liquids is nearly always accompanied by varying amounts of aqueous fluids present in the producing formation in conjunction with the hydrocarbons and/or condensed as the fluids flow from formation to surface equipment. These fluids usually contain dissolved gases such as H_2S , CO_2 and even low molecular weight water-soluble fatty acids such as acetic and propionic. All of these constituents make the produced water or brine corrosive to the steel equipment employed in oil and gas production.

Depending on the relative amounts of water and hydrocarbons and other factors specific to the individual wells and producing systems, the equipment may be wetted by either the aqueous phase, in which case corrosion can be expected, or by the hydrocarbon phase, in which it is not. Use of reverse-wetting inhibitors allows for the chemisorption of an inhibitor film as previously described, and this film then attracts additional hydrocarbon from the oil-phase of the flowing fluids to give water repellance and corrosion protection of the metal. A wide variety of materials, usually based on fatty amines and acids, is being successfully employed in petroleum production. The principal problem in the use of these materials is a technical one - application of sufficient chemical to the areas where it is needed. The technology to solve this problem is beyond the scope of this paper but is adequately described in the references cited.

By means of surface equipment, most of the aqueous fluids are separated from the hydrocarbons before the hydrocarbons are sent on through pipelines, etc., to refineries; however, a sufficient amount of water may remain to cause corrosion in the pipelines, and inhibitors can be applied for pipeline protection. When the crude, containing but small amounts of brine reaches the refinery, desalting equipment is employed to remove these small amounts before the oil is sent to the crude stills. Such equipment will remove 90% plus of the occluded salts from the charge to the stills; however, the small amount remaining still causes trouble. Under the operating conditions of the crude still and subsequent down-stream processes, decomposition of the residual calcium and magnesium chlorides not removed by the desalter gives gaseous HCl which results in an aqueous acid in the still condensers. The condensate may have a pH as low as 3, and is very corrosive to steel and to a lesser extent to copper equipment it contacts. Corrosion is effectively controlled by use of neutralizing amines such as ammonia, morpholine and proprietary compounds previously discussed and/or by use of filming amines, often based on the cyclic base imidazoline. By suitable adjustment of the pH to a value slightly below neutral, treatment costs can be minimized, and the dangers of fouling from amine chlorides is reduced.

H_2S formed by decomposition of sulfur compounds

also contributes to the corrosion problems in refinery units. A rough correlation exists between the total sulfur content of a "sour" crude and the corrosion load expected in processing equipment. The combination of neutralizer and film-forming inhibitor is also employed successfully versus H_2S corrosion. The presence of nitrogen compounds in the charge stocks often results in production of ammonia and HCN in the modern processes of hydrogenation. Aqueous condensates containing ammonia, H_2S , HCN , may be corrosive despite high pH values.

At pH values of about 9, corrosion rate of H_2S on steel is acceptably low and is limited by the formation of a semi-protective, insoluble iron sulfide scale. However, this scale is removed by HCN to form soluble ferrocyanide complexes, so that corrosion may be greatly accelerated. Special inhibitors have been developed to function under the high pH conditions and minimize the problem.

In all of the foregoing discussion, little mention has been made of the nature of corrosive attack or methods of measuring and monitoring it. The most widespread method in both laboratory and field is to use some sort of test specimen, generally called a coupon, composed of metal as similar in chemical and metallurgical properties as possible to the real metal it is desired to protect and placed in an environment as similar as possible to the corrosive environment. Parameters such as temperature, pH, fluid velocity, surface cleanliness, oxygen content, etc., are very important and are duplicated. The test coupons are weighed before and after exposure, and from the weight loss, the amount of metal removed is calculated on the basis of a uniform rate of attack expressed as inches per year or some similar unit.

Although the principle is universal and convenient, it has serious draw-backs, the chief one being that attack in real systems which result in corrosion failure is rarely uniform; rather do a few isolated spots generally experience attack much greater than the average uniform calculated rate, and failure occurs at one or more of these severely attacked areas. We have already mentioned pitting attack in the discussion on use of chromate inhibitors in cooling water systems. Another type of non-uniform attack occurs in refinery equipment in contact with H_2S and especially with H_2S and HCN . Such attack is evidenced by hydrogen blisters and distortion of ductile metals, while brittle failure due to hydrogen embrittlement may occur with metals of low ductility.

The explanation of the problem is given by Equation (4) for the cathodic reactions of hydrogen evolution. Under "normal" conditions, atomic hydrogen formed by primary attack of acids on active metals is rapidly and completely converted to molecular hydrogen. However, in the presence of many sulfur compounds, including H_2S , and nitrogen compounds, including HCN , the atomic hydrogen conversion is poisoned so that appreciable amounts of it can exist on the corroding metal surface. Since steel is permeable to atomic hydrogen, some of the atomic hydrogen can diffuse into the metal. Some of the hydrogen which diffuses will convert to molecular hydrogen at various grain boundaries, carbide inclusions, etc. However, under the conditions of temperature and pressure in refinery work, steel is impermeable to molecular hydrogen which can build up to pressures of several thousands of atmospheres in the hydrogen bubbles formed within the metal. This pressure may be relieved and evidenced by formation of

a blister if the metal has sufficient ductility. Otherwise, failure occurs due to so-called hydrogen embrittlement.

This problem has also been solved by the use of film-forming inhibitors which prevent the original corrosion reaction which allows formation of the atomic hydrogen and starts the chain. A word of caution is that many nitrogen-based inhibitors can actually increase the amount of atomic hydrogen present and thus accelerate the hydrogen blistering or embrittlement even though overall metal loss is reduced. The proper inhibitor must be chosen for the service.

A similar problem occurs in acid-pickling work where effective inhibitors for control of overall weight loss have been found to accelerate hydrogen uptake. The presence of arsenic, antimony and phosphorus compounds may also cause hydrogen problems.

FUTURE DIRECTIONS IN CORROSION INHIBITION There are many other industries and current applications of corrosion inhibitors which will not be discussed here. Some of the disadvantages of controlling corrosion by inhibitors include temperature limitations and specific action of the inhibitor. An example of temperature limitation is given in oil-well acidizing in which the problem and its solution are similar to those in acid pickling.

However, temperatures and contact times are much higher and it has taken considerable effort to develop inhibitors which are effective under the increasingly difficult conditions in using them in deeper and deeper oil wells. Similarly, in refinery and chemical processing work, inhibitors appear to break down and/or be ineffective at temperatures in excess of about 250°C.

Inhibitors in the sense in which we have discussed them are of no value for prevention of the attack on metals by corrosive gases. The so-called "vapor phase inhibitors" are generally salts of certain amines (e.g. cyclohexylamine nitrite) which act to inhibit the reaction of condensed water vapor which may contain dissolved gases causing the corrosion of steel, aluminum, etc., during storage at high relative humidity.

Most inhibitor applications are for protection of steel although some important work has been done for systems containing copper, aluminum, zinc and/or lead. More often than not the action of the inhibitor is highly specific and an inhibitor which is effective for one metal may be ineffective or even accelerate attack on another. When two or more metals are in the same system, particularly when they are electrically connected, the problem may be very difficult. Sometimes a combination of inhibitors is effective, e.g., chromate for steel and benzotriazole for copper as previously mentioned. Such applications are best proved by careful field studies.

The successful inhibition of automobile radiator fluids has necessitated the development of formulations which protect steel, brass, aluminum and lead (solder). Spin-off of this technology should be useful in assuring the reliable operation of solar hot-water units which have similar conditions and corrosion problems.

One of the principal advantages of chemical inhibitors as compared to other methods of corrosion control such as use of protective coatings or highly-resistant metals is that high capital costs are not needed for use of inhibitors; furthermore, the costs of inhibitor treatment may often be treated as expensed items - an advantage for tax and accounting purposes. The variety of available materials and the ease of treatment monitoring by coupons and more sophisticated electrical methods not discussed in this presentation make the probability of failure of an inhibitor systems and the cost of such a failure less with inhibitors than with coatings or metallur-

gical approaches. This variety and ease of monitoring also make it possible to vary the inhibitor, its treatment concentrations, treatment application points, frequency of treatment, etc., all of which give operating personnel advantages in attacking corrosion problems in situ.

Much good work on corrosion fundamentals and inhibitor evaluation is being carried out in university, governmental and industrial research and development organizations, and is helpful toward a better understanding of the problems and optimizing their solutions. However, it is the opinion of this speaker that few, if any, fundamental laboratory studies have led to the development of successful field treatments. These still require empirical approaches and reliable plant operating data.

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INFLUENCE OF MATERIALS SELECTION AND DESIGN ON CORROSION BEHAVIOR

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ABSTRACT

All engineers are involved in or affected by materials selection. Standardized techniques have been developed to make the process more efficient. A combination of these techniques plus a knowledge of the problems and consequences of corrosion should be important to improving of the general process and can result in significant savings for industry and government.

REGARDLESS OF THEIR engineering specialty, all engineers concerned with hardware of any sort (and this includes virtually all engineers), must deal constantly with the question of what material should be selected for construction of some particular piece of hardware. Except in trivial applications, it is not enough merely to indicate that the part should be constructed of "steel" or "aluminum" or "plastic". Instead, the engineer must be skilled at focusing his engineering knowledge upon the design and operational requirements of a particular part so that they may be adequately translated into purchasing specifications for specific alloys, finishes, heat treatments and so forth. Due consideration must be given not only to the mechanical aspects of design, but also must include consideration of corrosion resistance, safety, product degradation, expected life, salvage value, appearance, equipment available for fabrication, joinability, effect on the environment, energy costs, availability of strategic materials, production capacity (for major applications), availability of replacement or repair materials on short notice, required rate of return on investment, depreciation practice, tax consequences, product liability considerations, etc. The process can be exceedingly complex. However, it is amenable to organization into a generalized methodology which can simplify the process greatly.

The subjects of materials selection and corrosion are closely connected. A report entitled "The Economic Effects of Metallic Corrosion in the United States" was issued in 1978 (1*). This report concluded that the total costs of corrosion in the United States for the year 1975 amounted to approximately \$70 billion or 4% of the gross national product (GNP). Of this total about \$10 billion, or 0.6% of the GNP were considered to be avoidable costs. Thus, with adequate education and technology transfer, it should be possible to avoid approximately 15% of the present costs of corrosion. This then represents the immediate opportunity for those concerned with materials selection.

THE PROCESS OF SELECTION

Clauser et al. (2) have reviewed the overall process of materials selection in a series of short articles combined under the general title "How Materials

are Selected." As Clauser points out the task of making a sound, economic choice of engineering materials is not an easy one but is nonetheless one of the most important requisites to the development and manufacture of satisfactory parts at minimum cost. While there is a huge and growing literature on materials and their general application, there often is a lack of complete facts on which to operate when making specific choices.

Until the last two decades, materials selection was largely a matter of past experience, and engineers tended to make everything out of the few materials with which they were familiar. This practice continues today, however, there is an increased awareness of the inadequacy of this practice. The tremendous increase in the variety of materials, together with the need to accommodate new and more severe service, ecological and energy requirements at minimum cost, have forced the development of a rigorous engineering approach to materials selection. The recent history of ever-mounting awards in products liability lawsuits adds another important consideration when choosing materials of construction.

The so-called "scientific method" lists the major steps in the solution of engineering problems. They include

1. Analysis of the problem
2. Formulation of alternative solutions
3. Comparison and evaluation of alternatives
4. Decision.

In the context of materials selection these steps become

1. Defining the functional and service requirements of the materials of construction
2. Narrowing the field of choice to a few candidate materials
3. Comparing and evaluating the candidate materials
4. Making the final choice.

DEFINING THE MATERIALS REQUIREMENTS

At this stage in the process it is essential to identify and define the specific functions which are to be performed. What is the part supposed to do? The practices of "Value Engineering" (3,4) have broad application in this process. The detailed functions need to be identified carefully. For example, an automotive exhaust system performs a number of functions including

1. Conducting engine exhaust from the engine
2. Reducing noise
3. Preventing noxious fumes from entering the automobile
4. Cooling the exhaust
5. Reducing exposure of body parts to corrosive vapors and gases
6. Several others.

The providing of these functions imposes special materials requirements, including

*Numbers in parentheses designate References at end of paper.

1. Resistance to corrosion by CO, CO₂, SO₂, H₂SO₄ (from catalytic converter), H₂O, Pb, Br in the exhaust vapors
2. Resistance to corrosion by atmosphere, road salts, mud, etc., at various temperatures
3. Ability to be formed into intricate shapes
4. Weldability and ease of assembly
5. Availability in large quantities
6. Relatively low cost
7. Ability to be coated (for some alternatives)
8. Others.

SELECTING OF CANDIDATE MATERIALS

The problem of selecting candidate materials becomes a matter of evolving a basis for narrowing the field of choice from the thousands and thousands of potential choices, to the relatively few (three or four at the most) actual candidate materials.

To do this it is necessary to translate the functional and materials requirements into materials property terms (5). This implies a need for an inventory of materials properties.

A number of technical societies, trade associations, journals, and industrial firms have responded to the need. For example, the American Society for Metals has made an outstanding contribution with the publication of its new series of METALS HANDBOOKS (6). Table I is a partial list of "resource references" the author has found particularly useful in conducting the course in Materials Selection at the University of Florida. This list grows each year.

For parts subject to uniaxial tension it is simple to connect tabulated data to functional requirements since tensile strength data are readily available. However, for many actual service conditions there is no direct or simple correspondence with tabulated materials properties, and considerable creativeness is required in establishing a data base with which to evaluate and compare materials (5,6). Often it is helpful to combine tabulated properties for the sake of comparison, e.g., strength/density ratio, \$/psi T.S., etc. Figure 1 shows some typical formulas based on cost for performance.

TYPICAL FORMULAS BASED ON COST FOR PERFORMANCE*

Type of Structure and Loading	Relative Cost for	
	Equal Strength	Equal Stiffness
Rectangles in Bending	$(\frac{Y_{S1}}{Y_{S2}})^{1/2} \times \frac{P_1}{P_2} \times \frac{P_2}{P_1}$	$(\frac{E_1}{E_2})^{1/2} \times \frac{P_1}{P_2} \times \frac{P_2}{P_1}$
Solid Cylinders in Bending	$(\frac{Y_{S1}}{Y_{S2}})^{1/2} \times \frac{P_1}{P_2} \times \frac{P_2}{P_1}$	$(\frac{E_1}{E_2})^{1/2} \times \frac{P_1}{P_2} \times \frac{P_2}{P_1}$
Solid Cylinders in Tension	$(\frac{Y_{S1}}{Y_{S2}})^{1/2} \times \frac{P_1}{P_2} \times \frac{P_2}{P_1}$	$(\frac{E_1}{E_2})^{1/2} \times \frac{P_1}{P_2} \times \frac{P_2}{P_1}$
Solid Cylinders in Tension	$(\frac{Y_{S1}}{Y_{S2}})^{1/2} \times \frac{P_1}{P_2} \times \frac{P_2}{P_1}$	$(\frac{E_1}{E_2})^{1/2} \times \frac{P_1}{P_2} \times \frac{P_2}{P_1}$
Solid Cylinders as Columns	$(\frac{Y_{S1}}{Y_{S2}})^{1/2} \times \frac{P_1}{P_2} \times \frac{P_2}{P_1}$	$(\frac{E_1}{E_2})^{1/2} \times \frac{P_1}{P_2} \times \frac{P_2}{P_1}$
Cylindrical Pressure Vessels	$(\frac{Y_{S1}}{Y_{S2}})^{1/2} \times \frac{P_1}{P_2} \times \frac{P_2}{P_1}$	—

*Y_S = yield strength, psi; E = Young's modulus, psi; P = density, lb/in.³; P = price, \$/lb.

Fig. 1

In the case of exhaust system, above, considerable tabulated information exists, for example,

1. Corrosion data for metals and ceramics in the presence of exhaust gases
2. Weldability data for metals
3. Formability data, e.g., bend radii, etc.
4. Price information
5. Availability information
6. Mechanical properties at various temperatures.

From this data it is relatively simple in the case of the exhaust system to narrow the choice down to three or four materials which can then be compared in minute detail and the choice can be optimized in accordance with manufacturing, marketing or other objectives.

For complex systems weighted performance indices have been employed. When used with care such indices can be very helpful since each individual property can be weighted in accordance with its importance. NASA developed such a weighted index for use in selecting materials for the SST (2), Fig. 2. The processes of selection are amenable to computerization where the cost justifies.

PARAMETERS FOR THE SST MATERIALS RATING

Go-No-Go Parameters

Corrosion
Weldability
Brazability

Nondiscriminating Parameters

Availability
Producibility

Discriminating Parameters

Strength
As Welded Strength
Fatigue
Stiffness
Thermal stress
Toughness
Stability
Cost

WEIGHTED INDEX RATING CHART FOR SST MATERIALS

MATERIAL	GO-NO-GO * SCREENING			RELATIVE RATING NUMBER (O RATING NUMBER X *WEIGHTING FACTOR)								MATERIAL RATING NUMBER	
	CORROSION	WELDABILITY	BRAZABILITY	STRENGTH (5)*	TOUGHNESS (5)	STIFFNESS (5)	STABILITY (5)	FATIGUE (4)	AS WELDED STRENGTH (4)	THERMAL STRESS (3)	COST (1)	Σ REL RATING NO	Σ SIGMA RATING FACTORS
ALLOY AND CONDITION													
RENE 41													
AZ86													
INCONEL W													
WASPALLOY													
L605													
D979													
N155													
V36													
INCO 718													
INCO 901													

*WEIGHTING FACTOR (RANGE = 1 POOREST TO 5 BEST)
O RANGE = 1 POOREST TO 5 BEST

* CODE = S = SATISFACTORY
U = UNSATISFACTORY

Fig. 2

DESIGNING TO PREVENT CORROSION

There are a number of literature references dealing with design to prevent corrosion, for example, Mears and Brown (7). The first consideration in the design of a structure is to provide adequate mechanical strength. However, it usually also is desired that the structure remain serviceable for some minimum period of time. Thus, factors such as fatigue, creep, certain metallurgical transformations, and corrosion must be taken into consideration. Of these, corrosion may be the most complicated since the rate of corrosion depends on so many external factors. The designer's response to this problem may range anywhere from disregarding the problem altogether to providing extra section thickness as a corrosion allowance. Some understanding of the factors which influence the corrosion behavior of metals however, will be useful to

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designers in analyzing the problem. Corrosion is the reaction of a metal with its environment and can be either chemical or electrochemical. Since neither metals nor their environments are completely homogeneous, a number of electrochemical processes are possible (3). The designer has little control over the homogeneity of metals although he does have freedom of choice in specifying which alloys and specifications are applicable. While there are examples of failure of structures as the result of manufacturing defects in metals, a far more frequent problem is dealing with inhomogeneities in the environment. One of the most

commonly encountered such inhomogeneities of the environment is the development of corrosion cells resulting from local potential differences caused by concentration cells. For example, if one portion of a metal is in contact with a dilute solution and another portion of the same surface is in contact with a concentrated solution of the same substance, a difference in electrode potential may be observed and localized corrosion may occur on one of the areas. A special case of the concentration cell is the oxygen concentration cell. Such cells are caused by local differences in the oxygen concentration in various parts of the liquid

contacting the metal surface. It is usually observed that the portion of the surface contacted by the solution containing more oxygen is the cathode and is partially or completely protected.

There also are corrosion cells set up by local differences in temperature, agitation, illumination, liquid velocity, and in fact by almost any heterogeneity in exposure conditions (8).

Another important cause of corrosion is contact of dissimilar metals (or alloys). It often is necessary to select dissimilar metals to work together for mechanical reasons (e.g. to avoid galling or seizing, etc.). Where dissimilar metals must be used, attempts should be made to select materials whose electrode potentials are as nearly the same as possible in the expected electrolyte at operating temperature. In addition, the exposed area of the cathodic member of the dissimilar metal couple should be made as small relative to the size of the anodic member as is feasible so as to reduce the anode corrosion current density.

It is important to consider the character of attack which occurs and its influence on the function performed by the structure. Unfortunately, much corrosion literature merely reports what is described as a "corrosion rate" (e.g. mils per year). If that rate is calculated by change in weight of a specimen it is important to know the manner in which metal was lost. For example, if all of the corrosion occurred at a few localized areas, the calculated rate of corrosion based on weight change might be extremely low but the metal may actually have been perforated. For applications involving tanks or containers, such localized attack would lead to failure. By contrast the same degree of attack occurring at the neutral axis of a structural member would not be disabling.

Certain alloys may be sensitized to intergranular attack by local thermal treatments such as welding. "Weld decay" of certain austenitic stainless steels and the analogous phenomenon on certain of the aluminum-magnesium alloys are examples of such behavior. Materials selection must take into account the likelihood of occurrence and the consequences of such phenomena in choosing materials of these three classes for service.

A number of methods are available for alleviating corrosion. For example, in the case of galvanic corrosion, one may select combinations of metals and alloys which are known to develop little galvanic action under service conditions. Alternatively, the metals or alloys may be completely isolated from one another electrically. In some cases, galvanic action may be mitigated by the application of suitable paint coatings or by the use of galvanic anodes either in the form of discrete anodes or as sacrificial metal coatings, such as galvanizing on steel or alclad coatings on aluminum alloys.

Contact between metals and non-metals may cause special action on the metal in some circumstances. If the non-metallic material is capable of absorbing and holding moisture against the metal surface, serious corrosion may result from oxygen concentration cells or chemical concentration cells. This type of corrosion may be prevented by selecting non-metallic materials known to be relatively innocuous or by designing the equipment so that the non-metallic materials are not likely to become wet or will dry out rapidly. The provision of air circulation and good drainage is particularly important in these circumstances. Painting of metal surfaces or the use of heavy protective coatings of suitable adhesives or the impregnation of the non-metallic material with inhibitor compounds are other useable techniques.

In general, it is good practice to provide adequate drainage so that moisture and dirt do not accumulate on metal surfaces resulting in concentration cells. Crevices should be avoided if feasible thus it may be preferable to use butt-welded joints rather than lap

joints. If lap joints must be used, they should be carefully sealed to avoid ingress of moisture. Supports for storage tanks should be designed so that moisture will not be drawn under the tanks, between the tank and the supporting base. The use of "drip aprons" around the edges of tanks can reduce the tendency for rain water and spillage to accumulate under tanks. Parts such as pipe sections and heat exchanger bundles often can be designed so that certain portions may be easily replaced with a minimum of down time. Redundant parts may be desirable for parts requiring frequent shut down for maintenance or replacement. Flow systems should be designed with attention given to hydraulic design to avoid flow-related damage at changes in direction of constrictions. There are numerous other design considerations but these serve to illustrate the complexity of the problem.

Another aspect of materials selection which has assumed major proportions is the considerable increase in litigation for product liability. This has provided added urgency to proper materials selection to avoid corrosion failures. For example, recently a major manufacturer of recreational boats and motors brought out a new model of pleasure boat with "outdrive" propulsion. The engine was in-board but the rudder and propeller drive mechanism were outside the boat enclosed in a cast-aluminum housing. Steering effort was transmitted to the rudder via a set of gears consisting of a large "bull" gear (directly connected to the rudder) and a "worm" gear which activated the bull gear. The worm gear was supported by a bronze bushing which in turn was held in place within the aluminum housing by a stainless steel snap ring which fitted into a machined groove in the aluminum housing. The bronze bushing was separated from the aluminum housing by an O-ring which also served to seal against oil leakage. No protective coating was applied to the weather (out-board) side of the bronze bushing. Aerated sea water regularly splashed on the bronze bushing causing corrosion products from the copper-base alloy to wash down onto the aluminum housing and into the machined groove which contained the stainless steel snap ring. Copper plated out on the aluminum, setting up galvanic cells between aluminum and copper in the presence of salt water. The corrosion products of aluminum occupy much greater volume (perhaps 15 times as much) as the metal from which they are formed. The voluminous corrosion products compressed the snap ring so that normal vibration during operation of the boat resulted in its loss overboard. Without the snap ring to retain it, the bronze bushing also was lost overboard and with it, control of steering. At the time, the boat was travelling at 30 to 35 knots. With loss of steering, the trim tabs forced the boat into a tight circle throwing two passengers into the water where the boat passed over them, killing one and seriously injuring the other. The case was settled out of court for a substantial settlement. The design was improved considerably by substituting a combination stainless steel/bronze bushing for the previously all-bronze bushing. With the new design, no bronze was exposed to oxygenated sea water. A further improvement could be made by coating all the exposed parts (i.e. bushing, groove, etc.). Clearly, this is an example of the importance of good materials selection, and the consequences of inadequate assessment of corrosion possibilities.

ECONOMICS

Engineers need a firm grounding in the techniques of economic analysis of engineering problems. A working knowledge of the concepts of discounted cash flows, equivalent annual costs, and the effects of taxation are basic to the comparison of engineering alternatives. Such considerations are vital in selection of materials. The National Association of Corrosion Engineers has prepared NACE Standard RP-02-72 which suggests a number

of standard ways for the solution of economic problems involving corrosion. Stephens and Verink (9) have presented solutions to the examples given in the NACE specification using traditional economic analysis methods rather than the specific methods suggested by NACE. The traditional methods will be particularly useful to those who have formal training in engineering economy.

CONCLUSION

All engineers are involved in or affected by materials selection. Standardized techniques have been developed to make the process more efficient. A combination of these techniques plus a knowledge of the problems and consequences of corrosion should be important to improving of the general process and can result in significant savings for industry and government.

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CLASSES OF WEAR

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ABSTRACT

Materials wear away by several mechanisms. Several laws of wear are widely known but there is no law or model that includes very many of the parameters that are known to influence wear. Oxidative wear may be included with abrasive wear and adhesive wear when the scale of oxide film thickness is considered.

THE WEARING AWAY of surface materials by mechanical interaction is usually thought to be due primarily to either abrasion or adhesion. The abrasive mechanism of wear is most convincingly proven in systems containing "gritty" or "abrasive" "third bodies" or hard protruberances which leave scratches on the rubbing surfaces. It is a relatively straightforward exercise to show that the removal rate of surface material by the abrasive mechanism should be directly related to the average contact stress between surfaces and the distance of sliding in unit time (velocity). The removal rate should also be inversely related to the resistance of one or both sliding bodies to penetration by the third body. Hardness is taken as the measure of resistance to penetration. Thus we have a linear law of abrasive wear, (Kruschov and Babichev, (1*))

$$\gamma \propto \frac{WV}{H} \quad (1)$$

where γ is the time rate of removal, or wear, W is the applied load, V is the sliding speed and H is the pressure hardness of the sliding bodies.

The adhesive mechanism of wear became a credible concept during the years of development of the adhesive mechanism of friction. It also explains a number of types of surface distress in systems in which the presence of abrasive third body species is not obvious. Types of adhesive wear include galling, scuffing and seizure. Archard (2) has modeled the adhesive wear process in terms of the probability of collision and adhesion of the asperities on opposing

surfaces during sliding. The adhered asperities fracture at a different location than at the original interface leading to removal of surface material. The outcome of Archard's model is that wear rate is proportional to the probability of collision which is related to sliding speed, and related to the ratio of applied load to pressure hardness, i.e.,

$$\gamma \propto \frac{WV}{H} \quad (2)$$

There are obviously very many other expressions or laws of wear. The above laws were selected to illustrate the point that when considering few enough variables it is possible to derive very simple laws, and simple laws are very attractive. One interesting result of the above expressions of wear rate is that today one finds debates in the literature on whether a linear wear rate in practice is proof of abrasive or adhesive wear.

Part of the differences of opinion on the abrasive and adhesive mechanisms of wear is a matter of semantics, and part is due to the perspective of the observer. Perhaps the major difficulty is that there is inadequate agreement on whether the terms "abrasive" and "adhesive" should refer to the phenomenological or to the fundamental aspects of wear. In essence, the words themselves are too limited to cover the broad range of events on rubbing surfaces.

The phenomenological approach takes account of the environment in which the wearing parts are operating and emphasizes the general appearance of the worn surface. In the fundamental approach the important questions relate to the actual cause of surface alteration and material loss. Thus, grooves may form on a rubbing surface, which to some is adequate proof of abrasion but which upon closer examination may prove to be due to adhesion.

Part of the limitation of the term "abrasive" and "adhesive" may result from the implication in the use of these words that each type of wear operates exclusively and on every possible scale of size. To illustrate, first of all that several wear mechanisms exist and that a scale of size is an important perspective, the newly defined oxidative (or oxidation or corrosive) mechanism of wear is explained. This mechanism is easiest to define or justify in cases where the wear rate is readily influenced by controlling the partial pressure of oxygen (or sulfides, etc.) in the gaseous or liquid environment of the rubbing system. The general sequence of events in oxidative wear is that sliding contact removes oxides, and the oxides regrow only to be removed by later sliding contact.

THE OXIDATIVE MECHANISM OF WEAR

Oxides have long been known to influence wear rate of surfaces. The manner in which oxides influence wear rates is not known and thus the nature of an ideal oxide is not yet obvious. The partial pressure of oxygen in a gaseous or liquid atmosphere would probably influence the rate of oxide formation, the strength, tenacity and perhaps the form of oxide, but insufficient data are available on the specific effects. In general, oxides are thought to prevent seizure but oxides may also be abrasive. One of the first to publish work on the abrasiveness of oxides was K. Dies (3). Later J. F. Archard and W. Hirst (4) showed that even hardened steel is worn by oxides. J. R. Whitehead (5) found low friction at low contact pressure and high friction at high contact pressure between copper sliders, and attributed the low friction to the prevention of (local) seizure by an oxide film. A. W. Crook (6) gives an interesting summary of some wear studies and discusses the difference between severe wear and mild wear. J. K. Lancaster (7) has shown some of the details of the transition

*Numbers in parentheses designate References at end of paper.

between mild and severe wear. He uses as his starting point the previous conclusions that mild wear is a condition of inhibited severe wear. Severe wear is inhibited or prevented by surface contaminants, which prevent high traction stresses and thereby limit the growth of junctions. In unlubricated surfaces this limiting action is thought to be due primarily to the formation of oxide layers. These oxide layers are moderately firmly attached to the substrate but they may break away and become abrasive particles.

The next assumption is that the transition between the two forms of wear is controlled by a balance of, or competition between the rate of exposure of new surface (by oxide removal) versus the rate of covering the new surface with oxide. It would be expected that this transition would then depend on load, speed and ambient temperature. In fact, this was shown by N. C. Welsh (8) for steel. T. F. J. Quinn (9) has carried on some work on oxidative wear since the work of Welsh, but the subject received considerable attention at the Joint Conference on Chemical Effects at Bearing Surfaces in Swansea in 1971. Quinn (10) read another paper at the Conference as did S. W. E. Earles and N. Tenwich (11). (See comments by G. A. Berry (12) and response by Earles and Tenwich (13)). Finally, Quinn and J. L. Sullivan (14) gave a review of oxidation wear. The essential part of their model is:

$$\gamma \propto A \left(\frac{a}{U} \right)^{\frac{1}{2}} \frac{e^{-\left(\frac{Q}{RT_c} \right)}}{t_c} \quad (3)$$

where γ is the wear rate, A is the real area of contact over which wearing occurs, T_c is the temperature in the contact area, (a/U) is a time of oxidation where a is the radius of the average asperity contact region and U is the sliding speed, Q is the activation energy of oxide formation and t_c is the critical thickness of oxide film at which point the oxide breaks off. Encouraging correlation between the model and experimental data is said to have been achieved. It is obvious however that the model is based only on the rate of oxide build up and implies that the mechanism of loss of oxide is of no consequence. The authors claim that the only impediment to further application of their model is a lack of clear definition of the number of asperities in contact and the critical thickness of the oxide film. A careful review of the model casts some doubts on most of the quantities such as A , a , and T_c .

The oxidation mechanism of wear is important, and in fact, it may be the predominant mode of wear in all long lived systems. Further study is warranted, although it is probably best to abandon the assumption of the critical thickness of oxide. Rather, it is likely that such quantities as the mechanical properties of oxide film and the tenacity of oxide film to the substrate be explored. These are likely to be different quantities for each metal and different again for each condition (i.e., temperature, oxygen or CO_2 partial pressure, etc.) of oxide formation. The mechanism is complex but there has been no research focusing on the important quantities except in the aggregate, i.e., by measuring the rate of wear. It seems appropriate therefore at some time in the near future to measure the mechanical properties of oxide films, their tenacity to the metal and their thickness in a wearing couple.

COMBINED MODES OF WEAR

The most important reason for studying oxidation and wear is that a proper understanding of wear mechanism will lead to a proper solution to the wear problem. If the abrasive and adhesive wear mechanisms were operative, either separately or in some combination,

the solution to the wear problem would be simple. To minimize abrasive wear there are two alternatives, i.e., either eliminate abrasive substances or increase the hardness of the surface to be preserved. To minimize adhesive wear it appears useful to increase hardness also, but the operative material change is probably a decrease in ductility which usually accompanies an increase in hardness. Oxidative wear on the other hand may be controlled by revising the mechanical properties of the oxide perhaps through the addition of trace elements in the substrate, or by addition of elements and compounds in the environments.

Another view of the combined modes of wear may be seen in Fig. 1 where a scale of size is given. Seven columns of combined wear modes are given. Column "g" shows a mode of wear that is specifically excluded from consideration under columns "a" through "f". Columns "a" and "f" are probably those that are defined by the classical use of the terms "abrasive" and "adhesive". It must be acknowledged however that many wearing parts show no solid evidence of either abrasion or adhesion. In fact a close look at worn surfaces at the highest magnification in microscopes often reveals nothing at all. No scratches, grooves, pock marks, strain lines or other evidence of contact appears and yet material has been worn away. The only plausible conclusion that can be derived from such study is that any existing surface feature must be smaller than the ability of the microscopes to resolve. In the case of the S.E.M. one instrument used has a resolution limit of 75 Å. If scratches and other marks did exist on the worn surface they must have been less than 75 Å in all dimensions, and that is the scale of the thickness of oxides. Thus it is reasonable to postulate various methods of removal of oxide, for example, by abrasive action and/or by adhesive bonding between the oxide on opposing surfaces. Columns "c" and "d" indicate modes of loss of oxide only, by abrasion and adhesion respectively. Columns "b" and "e" are combined modes in terms of the extent to which the effects of abrasion and adhesion extend beyond the oxide layer.

Figure 1 omits the mention of erosion and erosion-corrosion. Solid particle erosion would be classified as one abrasive action. Erosion as used in much literature could include the action of molten plastics on a die surface and the action of liquid with and without solid constituents. Erosion-corrosion often refers to a system in which soft products of corrosion are swept away by passing gases, liquids or even solid bodies, further corrosion occurs, etc.

The role of the products of oxidation and/or corrosion is not well understood. In some literature the oxide seems to be considered abrasive and in other literature it is ignored as a soft species to be removed from the system. Whether or not an oxide is "abrasive" may depend on the properties of the loose and the attached oxide. A loose oxide circulating in the system surely impinges upon and slides along attached oxide and could be the proximate cause of the loss of more oxide. The rate of removal of attached oxide may depend on the ductility of the substrate, size of loose oxide particles and many other factors. Many of these factors need further work.

DEBRIS ANALYSIS

In the study of wear the debris is sometimes studied. Debris analysis is very successfully done in conditioning monitoring of machinery (15). Tell-tale forms and amounts of debris accompany some particular modes of component degradation. Where clear adhesive or abrasive wear takes place, unique debris often appears. Unfortunately modes "b", "c", "d" and "e" in Fig. 1 produce finely divided oxides, which obscures the mechanism of wear. Even if some metallic

debris is formed the metal may oxidize before ejection from the system and from the debris it would be impossible to determine how the wear took place.

It is obvious that there are several mechanisms of wear, and equally obvious that a number of the relevant quantities for writing a complete law or model for wear have remained out of reach. It is also obvious that unless we know how wear occurs we will not be able to design materials and systems for long wear life.

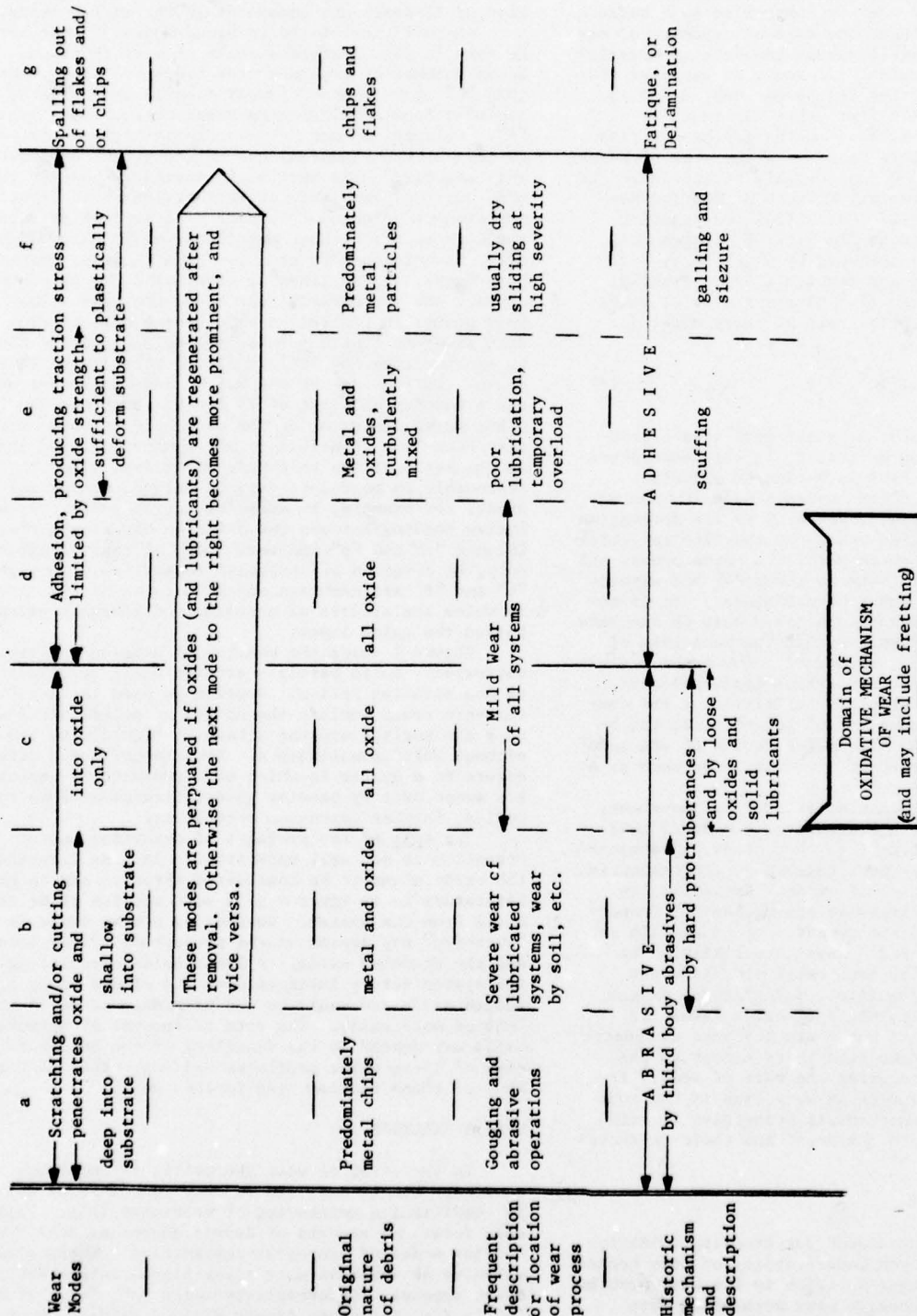


Fig. 1 - Modes and mechanisms of wear in dry and lubricated metallic sliding systems (oxides will include all solid surface reactive products including sulfides, etc.)

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DESIGN SOLUTIONS TO WEAR PROBLEMS,
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(Abstract and text were not provided for publication)

NOVEL LUBRICANTS - DEUTERATED MATERIALS WITH SUPERIOR PROPERTIES

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ABSTRACT

Over the past several years only incremental improvements have been made in the development of new and improved lubricants. Recently however, scientists at NADC (Warminster) have succeeded in demonstrating that deuteration of hydrocarbon greases has resulted in a startling 5-fold improvement in bearing life. Since oxidation is expected to play an important role in the degradation of lubricants, it is not surprising to find that the deuterated material was many times more resistant to oxidation than the normal hydrogen analogs. Moreover, the 5-fold improvement in bearing life for the 97% deuterated grease is entirely within the range expected for the well known isotope effect in classical chemical kinetics. Fifty-fifty mixtures of 97% deuterated fluid with the original hydrocarbon oil were significantly less oxidatively stable than was 50% randomly deuterated materials, suggesting that protecting selected chemical sites may be important in improving lubricant oxidation resistance.

BACKGROUND

Until World War II, with but minor exceptions, petroleum-based fluids provided almost all of the lubricants required by the technology of the period. They served adequately, both with respect to their availability and the performance required of them. For certain limited applications, however, natural products such as sperm whale oil for clock and instrument bearings requiring non-spreading lubricants were employed. With the quantum-jump increase in performance and reliability of power plants, instrumentation, etc., required by the wartime- and postwar-generated technologies, the traditional lubricants were found to be frequently inadequate. Two examples will serve to suffice--gas turbine engines and instrument guidance systems.

Lubricants for internal combustion aircraft engines probably experience temperatures not much more stringent than today's automobiles, i.e. bulk oil and cylinder wall temperatures of ca 100° and 235°C, respectively. Present aircraft gas turbine engines, on the other hand, operating under Mach-2 conditions generate bulk oil temperatures of 150°C, oil-out temperatures of 260°C, and under soak-back conditions when the engines are turned off, wall temperatures of 360°C. Such conditions far exceed

the capabilities of petroleum, and synthetic esters are now employed exclusively for this application. Temperature stability is generally a less significant requirement for lubricants for guidance and related instrumentation. Such gear is lubricated initially with minimal quantities of oil or grease which must last for the operational lifetime of the mechanism; even minor changes in viscosity, or the generation of organic particulates resulting from lubricant or additive package deterioration, can result in unacceptable instrument performance. A variety of lubricant base stocks are presently employed in these applications, i.e., petroleum oils, highly refined petroleum oils, modified silicones, esters and synthetic hydrocarbons. There is a need, however, for materials with improved performance, particular in those cases where they critically affect instrument life.

In the last several years only incremental improvements have been made in the development of new and improved lubricants. One novel approach has been generated by the use of deuterated fluids. Based on the deuterium isotope effect the authors at NADC have postulated and demonstrated, as shown below, that an instrument grease based on a deuterated synthetic hydrocarbon gave at least a 5-fold increase in a test bearing life as compared to that with the nondeuterated analog, and that the deuterated base stock was more stable than the undeuterated material (1,* 2). Based on this preliminary effort, NADC and NRL are preparing a joint program to investigate some of the fundamental reactions involved in the deuteration process and the reactions of classes of deuterated lubricants other than synthetic hydrocarbons, and to perform the necessary test and evaluation studies preparatory to field testing these materials.

THE DEUTERIUM ISOTOPE EFFECT

The deuterium isotope effect has been known to chemical kineticists for decades and hence is well documented. However, its value in lubrication has only recently been recognized. For an excellent review of this phenomenon the reader is referred to an article by K. B. Wiberg (3).

*Numbers in parentheses designate References at end of paper.

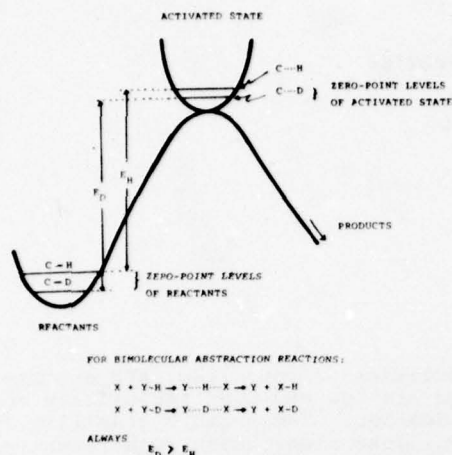


Fig. 1. - Isotope effect in bimolecular abstraction reactions

In Fig. 1 we show a simplistic schematic diagram of vibrational levels in a molecule, containing C-H(D) bonds undergoing chemical reaction. If it is assumed that this potential surface is virtually the same for both the normal and deuterated materials and that the vibrations approximate harmonic oscillation or Hooke's law, then the vibrational frequency of a species is simply dependent on the mass of the vibrating atoms (for C-H(D) bonds: $\nu_H/\nu_D \sim \sqrt{m_D/m_H} = \sqrt{2}$). For low or moderate temperatures the vibrational energy $E = 1/2 h\nu$, where h is Planck's constant. This is the so-called zero point energy. If the rate determining step in a molecular reaction is attack on the C-H or C-D bond, then absolute rate theory predicts that the reaction rate ratio is dependent on the difference between the activation energy $E_H - E_D$. If there is negligible difference in the zero point energy levels of the activated state, then:

$$\frac{k_H}{k_D} \approx e^{(E_H - E_D)/RT} \approx e^{(h\nu_H - h\nu_D)/2RT} \quad (1)$$

where k is the reaction rate, R is the well known gas constant and T is temperature ($< 800^\circ K$). However, at higher temperatures $k_H/k_D \rightarrow \sqrt{2}$. For typical vibrational C-H(D) stretching frequencies $k_H/k_D \sim 5$ for ambient conditions, which is nearly identical to the lubricant lifetime improvements found in deuterated greases, as will be shown in the next section.

There are innumerable experimental examples of the isotope effect. The rate factors (k_H/k_D) range from ~ 2 -10. The lower values are likely due to differences in the activated complex which will diminish in part the difference in activation energy of the C-H and C-D reaction paths. On the other hand quantum mechanical tunneling enhances the reaction rate ratio because the more energetic species (C-H) can penetrate the potential barrier at a greater rate than predicted by classical theory, hence the wide range in rate ratios.

As indicated above, the stability and performance of an instrument grease based on a synthetic hydrocarbon (derived from poly-

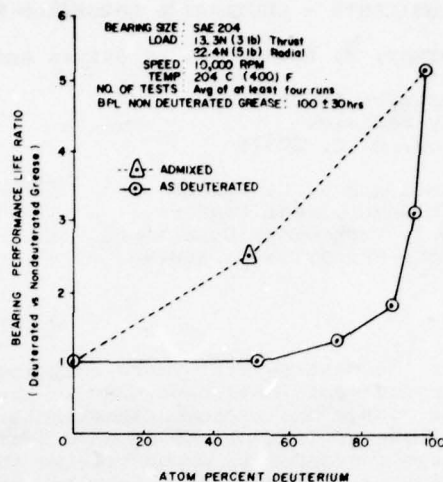


Fig. 2. - Anti-friction bearing performance life ratios of SH greases

merized olefins) in which 97% of the hydrogen was replaced by deuterium has been demonstrated (1,2). Fig. 2 shows that a 5-fold increase in test bearing life resulted as the deuterium content of the base hydrocarbon increased to 97 atom %, with the effect commencing at ca 73 atom %. Fig. 3 suggests that this remarkable increase in bearing life was due to the

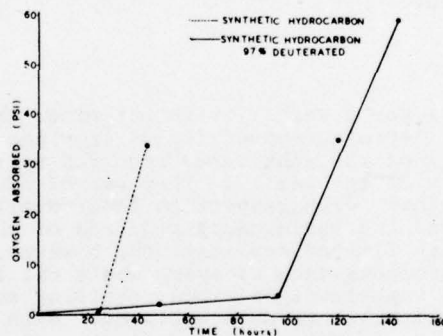


Fig. 3. - Fluid oxidation - Bomb oxidation method, antioxidant not added

improved oxidation resistance of the base stock, which was synergistically enhanced by the presence of an antioxidant, Fig. 4. It should be mentioned that the deuterated and normal compounds were prepared by identical methods in order to rule out any impurity differences in the stock compounds.

The results, however, were not entirely unambiguous. When equal volumes of nondeuterated and 97 atom % deuterated fluids were mixed to give an effective deuterium concentration of 49 atom percent, oxidation resistance was appreciably less than that of a 51 atom percent randomly

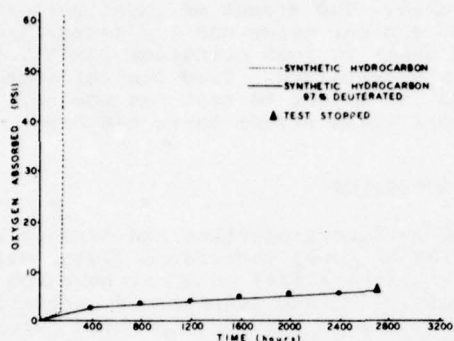


Fig. 4. - Fluid oxidation - Bomb oxidation method, antioxidant added

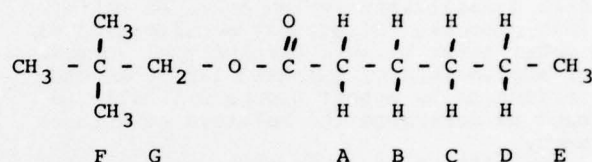
deuterated fluid. However, as seen in Fig. 2, performance of the grease based on the admixed fluid was better than that based on the 51 atom % deuterated material. While insufficient data are as yet available to resolve this anomaly, it is reasonable to assume that the more oxidatively labile sites in the 51 atom % randomly deuterated material were protected by deuterium substitution, which would not be true for the mixed fluids. The results of the bearing tests suggest that while oxidation stability of the lubricant may be an important factor in performance, other factors such as contamination, metal catalytic effects, etc. may also play a significant role in lubricant life and bearing failure.

FUTURE WORK

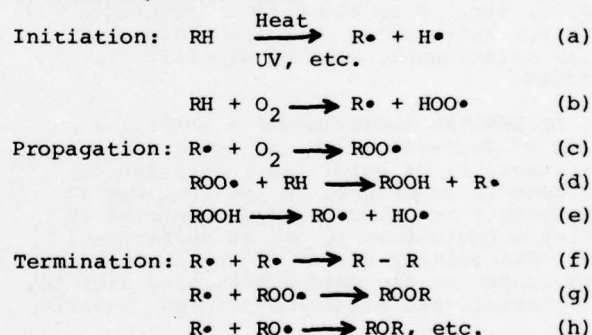
DEUTERATED HYDROCARBONS - Because of the very promising results indicated above, we are planning a vigorous program to investigate and exploit the full potential of these novel lubricants. Initially we shall examine various hydrocarbon oils and greases. Bearing tests, oxidation stability, impurities and effects on metal surfaces will be ascertained as a function of temperature. Several laboratories will conduct independent measurements on a variety of different species of full or partial deuteration (random and site-selected up to 99%D). A comprehensive examination of the economics for various applications will be carried out.

DEUTERATED ESTERS - Since esters generally represent a more realistic approach to most critical lubricant application, an important goal will be to deuterate and examine these materials. The following section describes this class of lubricants in more detail.

Because of their desirable extreme temperature viscometric and stability characteristics, polyol esters are frequently preferred to the earlier diester fluids. In a recent study (4) at the Naval Research Laboratory, the selectivity of the oxidative attack on a model neopentyl polyol ester was investigated. The ester, neopentyl hexanoate, was selected because it contains all of the groups found in the widely used commercial oils based on pentaerythritol esters, and because it was amenable to convenient analysis. The model ester structure is shown below:



In classical degradation mechanisms, the principal steps in the oxidation of hydrocarbons/esters are:



The more difficult the abstraction of the hydrogen from the original material RH (Reaction d), by the peroxy radical ROO \cdot , the slower the overall oxidation or degradation rate. Replacement of hydrogen by deuterium would be expected to slow down this rate. In general, the order of stability of carbon-hydrogen bonds is primary > secondary > tertiary. The model ester shown above contains primary and secondary, but no tertiary bonds. Sites of potential oxida-

Table 1 - Relative Oxidative Attack on the Various C-H Bonds in Neopentyl Hexanoate

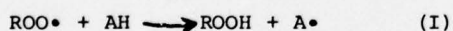
Type of C-H Bond	Sites	Method of Calculation	Relative Rate (Av. + Std. Dev.)
Primary	E,F	-	(1.00)
"Normal" Secondary	B,C,D	12 (B+C+D) / 6 (E+F)	15.2 \pm 1.4
alpha-Acyl Secondary	A	12A/2 (E+F)	1.8 \pm 0.2
alpha-Alcohol Secondary	G	12G/2 (E+F)	4.2 \pm 1.2

tion are given by the letters A - G, with E and F being primary bonds and the remainder secondary bonds. In Table 1, it is seen that the "normal" secondary bonds, B, C, D, are about 15 times more susceptible to oxidative attack than are the primary bonds, and that the remaining alpha-acyl and alpha-alcohol bonds are 2 and 4 times more susceptible, respectively.

We plan to selectively deuterate neopentyl hexanoate (or similar ester) to determine what degree of improvement in oxidation resistance results. In the above example, deuteration of the "normal" secondary hydrogens is obviously indicated as a first step. Isotope effect theory suggests that a perceptible increase in stability would be observed. The stability of the completely deuterated ester would also be of interest as it would be a measure of the ultimate intrinsic stabilization which could be achieved by this process. Structural modification of the model ester by more conventional routes, i.e., replacement of selected labile secondary hydrogens by methyl groups will also be pursued to determine the relative advantages of each.

The effects of deuteration on lubricant properties other than oxidation stability are also of practical importance. The isotope effect may be expected to affect flash and fire points, pyrolytic stability, surface tension, etc. From the data in reference (2) it is not anticipated that temperature-viscosity relationship will be significantly affected.

DEUTERATED ANTIOXIDANTS - While the effect of deuteration on the intrinsic oxidation stability of ester lubricants is unquestionably important, in the real world antioxidants are almost always employed in working formulations to extend operational life. The primary effect of the antioxidant is to interrupt the rate-determining step in the autocatalytic oxidation process (Reaction D):



Here AH represents an antioxidant with H being the active hydrogen. In general, the radical A is less reactive than R, thus slowing down the overall degradation process.

Some studies have been made of the deuterium isotope effect on an antioxidant activity (5) when deuterium is substituted for the active hydrogen. Since deuterium is less easily abstracted than hydrogen, it might be expected that the deuterated antioxidant should evidence diminished effectiveness. On the other hand it might be metered out more efficiently, and so last longer. It was found that in evaluating the effectiveness of amine-type antioxidants with butadiene-styrene copolymers, in which the active hydrogen was replaced by deuterium, the direction and magnitude of the isotope effect was influenced by (1) antioxidant concentration; (2) oxidation temperature; and (3) nature of the antioxidant. There may also be side reactions such as hydrogen-deuterium exchange which serve to obscure the isotope effect, or direct oxidation of the antioxidant to initiate new chains. To sort out these various parameters, we plan to prepare analogs of the widely used antioxidant

phenyl-1-naphthylamine in which the active hydrogen is replaced by deuterium in one case and all of the hydrogens are replaced in the second case. The effect of these antioxidants on a model ester and its deuterated analogs under various oxidation conditions would be ascertained. From the information obtained, we expect to sort out some of the parameters which affect these systems.

OTHER PROPERTIES

The surface properties and surface reactivities of these deuterated fluids will have a critical effect on their behavior as lubricants. Surface tension and wettability measurements will provide important information about the former. The orientation and reactivities of the fluids on metal and other surfaces will be investigated by Fourier Transform IR and ATR techniques.

Finally, to bring into proper perspective the role of deuterated fluids in practical applications, we plan to life-test selected mechanisms lubricated with deuterated fluids or greases. Because of their present high initial cost, these materials would be used in conjunction with systems requiring small amounts of lubricant, such as guidance gyro miniature bearings, actuating mechanisms, fan motors, etc. It is conceivable that at a later date, they might be tested in high temperature mechanisms, such as small gas turbine engines.

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NATIONAL PERSPECTIVES ON WEAR -- THE ALLOY QUESTION

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ABSTRACT

Metallurgical requirements for resistance to both metal-to-metal wear and abrasive wear can usually be defined in terms of microstructure. Alternative approaches can be developed to achieve the desired microstructures, including alternate alloys. Alloy combinations can be varied to provide the appropriate microstructure within practical limits of section size and heat treatment capability. Alloys can be used to alter the morphology and hardness of carbides in wear resistant high-carbon alloys. Hardness of the abrasive influences the microstructure required to resist abrasion. Practical wear resistant alloys must possess adequate toughness to withstand the service conditions.

METALLURGICAL CHARACTERISTICS of mating surfaces to resist metal-to-metal wear or of surfaces subjected to abrasive wear will be the focus of this paper. It has been observed that if the desired microstructure can be established, there are usually alloy systems that can provide that microstructure, thus providing alternative alloys for a given wear problem. Examples will be given of some alternative alloys and their possible limitations in terms of wear resistance or other properties that may influence performance.

Obviously, if a mechanical system is adequately lubricated, two opposing components should not wear. In machinery design this is the desired goal, and may be achieved during a large part of the operating life of the machine; but the small percentage of time that involves marginal lubrication under high unit loads, or interrupted lubrication, provides the conditions for concern about metal-to-metal wear. There are also many unit operations in which no lubrication is present. The mining and milling industry provides many examples. In these applications, controlled abrasive wear is encountered. Loss of metal from the work of comminution is expected to occur; the rate at which it occurs defines the period of operation before replacement parts must be installed.

METAL-TO-METAL WEAR

This section of the paper will be restricted to a few of the more common metallurgical systems used to combat wear under conditions of marginal lubrication. These examples will be sufficient to point out the opportunities for alternate alloy design.

CASE-HARDENED STEEL - The most frequent method of limiting loss of metal from two marginally lubricated mating steel surfaces is to provide high surface hardness. One way that this can be done is by introducing either nitrogen or carbon or both into the surface of low-alloy steels. This is done by diffusion processes at elevated temperatures. The objective is to provide surfaces that will not gall or seize, because once these incipient welding situations occur, wear accelerates rapidly due to transfer of load to adjacent

surfaces and to abrading of other portions of the surface by trapped wear debris.

Nitrided cases are harder (above 1000 HV), but very thin (about 0.4 mm) and can withstand only modest compressive load. This is compensated for by providing a supporting microstructure of tempered martensite in a steel which resists temper softening at the nitriding temperature, in the range 550 to 650 C, depending on the process employed. Steels used in nitriding usually contain 0.3 to 0.4% C to provide a strong but tough supporting structure, about 1% Al to aid nitrogen diffusion and to provide a higher hardness at the surface, and are usually alloyed with 0.5 to 1.0% Mn for hardenability, 1 to 1.5% Cr and 0.15 to 0.45% Mo. The chromium and molybdenum levels are chosen not only to provide hardenability (to assure a fully martensitic structure in the part after quenching prior to nitriding), but also because both alloys assist in retaining good hardness during tempering before final machining prior to nitriding, and during the nitriding process. Alternate alloys are limited because of the several metallurgical requirements mentioned above. Nickel and additional manganese can be used in place of part of the molybdenum, with some sacrifice to tempered hardness.

Carburized cases are deeper (ranging from 0.7 to 1.5 mm) resulting from processing at temperatures in the range 900 to 950 C prior to quenching. The structure comprises high carbon martensite (about 800 HV) at the surface, gradually reducing in carbon content and hardness until the base metal or "core" is reached. The case depth, core carbon content, and hardenability are usually selected on the basis of the mechanical properties and residual stresses required by the design. Techniques have been developed to tailor the alloy content of a part to meet the metallurgical requirements. These are discussed in detail in a series of articles by Breen and coworkers (1*). The system requires preselection of limits on each alloying element, based on known processing characteristics and property requirements. Once these limits are established, the computer provides a series of alternate standard steels or will suggest the lowest cost alloy combination. The system can be used, and has been used, in instances involving unavailability of a preferred standard steel.

HARDFACING ALLOYS - An effective method of combatting metal-to-metal wear under unlubricated conditions is hardfacing the working surfaces. These hardfaced deposits contain a substantial percentage of hard carbides in a matrix that resists galling and seizing. Some of the most effective hard-facing alloys are cobalt-based. In partial answer to the recent sharp increases in the price of cobalt, nickel-based alloys are being developed as substitutes. Such substitute alloys probably will need to be tailored to specific applications, because there does not seem to be a general understanding of the relative contribution of matrix strength, work-hardening characteristics and primary carbide hardness and morphology to the wear resistance of hardfacing alloys. A comparison of one such Ni-Cr-Mo-C alloy with a Co-Cr-W-C alloy, which has had wide usage, was recently described by Whelan (2). The cobalt base Alloy No. 6 contained 1.2% C, 29% Cr, 4.5% W; the nickel base Alloy XN-930C contained 2.0% C, 0.5% Mn, 1% Si, 30% Cr, 9% Mo, 3% Fe. Hardness values were the same at room temperature (416 HV) and at elevated temperatures the nickel-based alloy exhibited somewhat higher hardness. Wet sand abrasion test volume losses were nearly equivalent. In thrust washer wear tests against AISI M2 tool steel, wear volumes were less for the M2/XN-930C pair than for the M2/Alloy No. 6 pair in tests both at room

*Numbers in parentheses designate References at end of paper.

temperature and at 425 C, indicating superior performance for the tool steel/nickel-base alloy pairs. Field evaluations are currently in progress. It is likely that suitable nickel-based hardfacing alloys can be developed to function as effectively and at much lower costs than the cobalt-based alloys.

ABRASIVE WEAR

Both steels and white irons are used extensively in applications involving abrasive wear. Investigations over the years have revealed useful relationships between microstructure and resistance to abrasion. For most applications involving abrasive wear, the mechanical properties, particularly impact resistance, of the material must also be considered, and accommodated in the equipment design. The level of impact usually dictates whether a part can be made of steel or of white iron, although white irons are used in service which appears, at first, to involve high levels of impact loading. For example, white irons are used for hammers in impact crushers, Figure 1, and as concave liners in gyratory crushers, Figure 2. Needless to say, design parameters influence such applications, and unit forces are kept within the fracture strength of the materials of construction.

Table 1 - Hardness of Minerals and Microconstituents

Mineral	Hardness	
	Knoop ^a	HV
Talc	20	
Carbon	35	
Gypsum	40	36
Calcite	130	140
Fluorite	175	190
Apatite	335	540
Glass	455	500
Feldspar	550	600-750
Magnetite	575	
Orthoclase	620	
Flint	820	950
Quartz	840	900-1280
Topaz	1330	1430
Garnet	1360	
Emery	1400	
Corundum (alumina)	2020	1800
Silicon Carbide	2585	2600
Diamond	7575	10000
Material or Microconstituents		
Ferrite	235	70-200
Pearlite, unalloyed		250-320
Pearlite, alloyed		300-460
Austenite, 12% Mn	305	170-230
Austenite, low alloy		250-350
Austenite, high Cr iron		300-600
Martensite	500-800	500-1010
Cementite	1025	840-1100
Chromium Carbide (Fe,Cr) ₇ C ₃	1735	1200-1600
Molybdenum Carbide Mo ₂ C	1800	1500
Tungsten Carbide WC	1800	2400
Vanadium Carbide VC	2660	2800
Titanium Carbide TiC	2470	3200
Boron Carbide B ₄ C	2800	3700

^aTypical values.

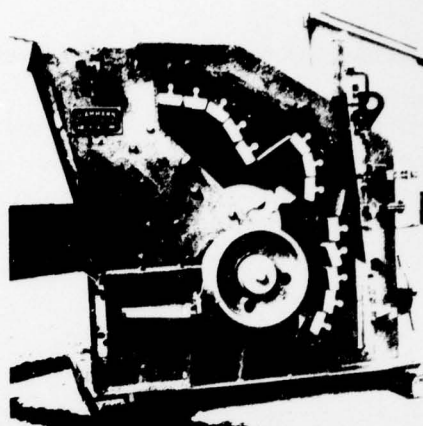


Fig. 1 - Hammer mill used for crushing limestone



Fig. 2 - Installing concave liner in gyratory crusher used for primary crushing of ore

INFLUENCE OF ABRASIVE HARDNESS AND MICROSTRUCTURE ON WEAR - The hardness values of microconstituents as well as the hardness of minerals which the abrasion-resistant irons and steels are used to comminute or contain are shown in Table 1 (3). White cast irons represent a composite of hard carbides and a metallic phase. In low-chromium white irons the carbide is cementite, M₃C, with a microhardness in the range 850-1100 HV. In irons containing more than about 10% Cr, the primary carbide is M₇C₃, with a microhardness in the range 1200-1600 HV. Newly developed white irons contain primary vanadium carbide, VC, with a microhardness of about 2800 HV. The metallic phases in these irons range from pearlite, with a microhardness in the range 250-450 HV, to austenite, with microhardness in the range 250-600 HV, to martensite, with a microhardness of 500 to over 1000 HV, depending on the carbon content, alloy content and the quantity of retained austenite.

One recent study demonstrated the influence of microstructure on wear by abrasives of differing hardness (4). A pin abrasion test, generally considered a high stress abrasion test, was used (5). In this test a cylindrical specimen moves back and forth in a non-overlapping pattern across a fresh abrasive cloth while under a load of 6.8 kg (15 lb). As it travels, the pin also rotates around its axis at 20 rpm. In 7 minutes the pin travels a distance of 12.8 m (504 inches). After a run-in, the weight losses in two successive tests are averaged. A photograph during tests is shown in Figure 3. The abrasives used were: garnet, with a microhardness of about 1400 HV; alumina, with a microhardness of about 1800 HV; and silicon carbide, with a microhardness of about 2600 HV. The steels and irons tested are listed in Table 2. Condition of the materials and their hardness and microstructure are given in Table 3. Wear, in terms of specimen weight loss, is shown in Figure 4 for each of the materials and abrasives.

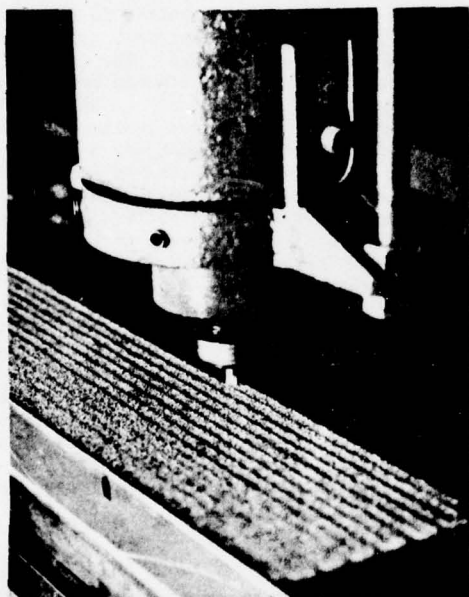


Fig. 3 - The specimen, specimen support, and the abrasive during pin abrasion testing

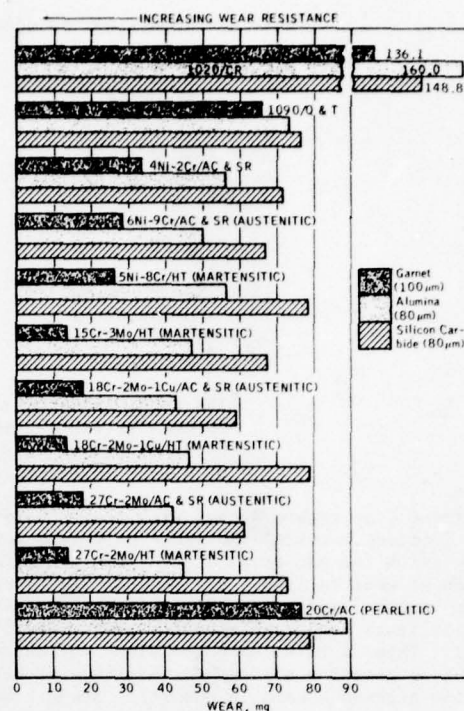


Fig. 4 - Influence of various abrasives on wear in a group of ferrous metals subjected to abrasion in the pin test

Table 2 - Chemical Composition of Steels and Alloyed White Irons

Alloy Designation	Element (%)						
	C	Si	Mn	Cr	Mo	Ni	Cu
AISI 1020 ^a	0.20	0.2	0.5	-	-	-	-
AISI 1090 ^a	0.90	0.2	0.7	-	-	-	-
4Ni-2Cr	3.36	0.53	0.49	2.0	0.14	3.90	-
6Ni-9Cr	3.22	1.77	0.55	8.9	0.04	5.86	-
5Ni-8Cr	2.85	1.67	0.46	8.2	0.07	4.86	-
15Cr-3Mo	2.79	0.50	0.66	14.5	2.58	-	-
20Cr	2.64	0.64	0.81	19.8	-	0.15	0.06
18Cr-2Mo-1Cu	2.96	0.52	0.79	17.5	1.55	-	0.98
27Cr-2Mo	2.65	0.48	0.83	27.1	1.87	0.16	0.06

^a Nominal composition

Table 3 - Condition, Hardness and Microstructure of Steels and Irons

Material ^a	Hardness (HV 30)	Predominant Microstructural Constituents
AISI 1020 CR	224	Ferrite and Pearlite
AISI 1090 Q and T	735	Martensite
4Ni-2Cr AC and SR	700	Austenite and M ₃ C
6Ni-9Cr AC and SR	433	Austenite and M ₇ C ₃
5Ni-8Cr HT	799	Martensite and M ₇ C ₃
15Cr-3Mo HT	828	Martensite and M ₇ C ₃
20Cr AC	398	Pearlite and M ₇ C ₃
18Cr-2Mo-1Cu AC and SR	496	Austenite and M ₇ C ₃
18Cr-2Mo-1Cu HT	780	Martensite and M ₇ C ₃
27Cr-2Mo AC and SR	558	Austenite and M ₇ C ₃
27Cr-2Mo HT	765	Martensite and M ₇ C ₃

^aThe condition of a material is identified by letter codes:
AC and SR, as-cast and stress relieved; CR, cold rolled;
HT, heat treated (by austenitizing and air cooling followed
by stress relieving); Q and T, quenched and tempered.

It is evident from Figure 4 that with a high hardness abrasive (silicon carbide) the range of weight losses is narrow (with the exception of the 1020 steel) and the amount of wear is high. When softer abrasives are used, the weight losses for the austenitic and martensitic white irons were significantly lower relative to the steel. This is to be expected since the hardness of the softer abrasive approached the range of hardness of the carbide phases in the white irons. Note, however, that garnet is hard relative to the steel microconstituents, and it abrades steel nearly as aggressively as alumina and silicon carbide. Garnet has been selected for most pin abrasion tests at the Climax laboratory because it more nearly represents minerals encountered in hard rock mining and milling.

The wear resistance of the white irons was greatly influenced by the metallic matrix structure. When garnet is used as the abrasive, the heat treated 15/27Cr-2/3Mo irons exhibit least wear. Next in abrasion resistance are the as-cast (austenitic) versions of the same irons. When alumina or silicon carbide is used, austenitic irons exhibit less wear than martensitic irons. The as-cast austenitic Ni-Cr irons are alternates that are considerably better than pearlitic 20Cr irons or steels free from primary carbides. In the event of chromium shortages, these lower chromium white irons will be favored.

Another white iron currently being investigated is one in which vanadium is the principal carbide forming element. The VC carbide is discontinuous and blocky, and preliminary tests indicate that higher toughness can be attained at high hardness levels in heat treated vanadium irons. A promising composition is one containing 2.6% C, 6% V, 3% Cr and 1.5% Mo. The chromium and molybdenum are required to achieve a martensitic matrix in the iron. The composition is more expensive than high-chromium irons at the present time and will be developed for certain specialized applications.

MICROSTRUCTURE CONTROL IN HIGH CHROMIUM WHITE IRONS - The alloy requirements to assure freedom from pearlite in 15/27Cr white irons have been studied extensively by Climax and by others. As was evident in Figure 2, large castings and many of them, are needed in ore crushing and grinding. Replacement of the castings results in undesirable interruptions in ore production as well as high cost in materials and labor. Alloys are costly, but it is even more costly to put a casting in service in a condition that will result in premature failure or rapid wear.

It has been possible to simulate in the laboratory the cooling rates in massive sections, using very small specimens in a quench dilatometer. The transformation kinetics can be observed on continuous cooling, and the microstructure and hardness of the as-cooled specimen can be measured. Continuous-cooling transformation diagrams have been determined for a series of 17.5% Cr irons containing additions of molybdenum, silicon, manganese, nickel and/or copper (6). Hardness of as-cooled specimens was also plotted as a function of log half-cooling time, a measure of cooling rate. One such extended "hardenability" diagram is shown in Figure 5. Superimposed on the diagram are half-cooling time values at the center of air cooled 50 mm diameter and 300 mm diameter rounds. Also, the 800 HV hardness line is dashed for emphasis. The objective in heat treating a white iron is to attain a hard martensitic matrix structure throughout the section, because in service the part may be worn well below the center of a section before it is discarded. Hardness at or above 800 HV usually results in the lowest wear rate, therefore it is an additional objective to attain that hardness in the martensitic irons.

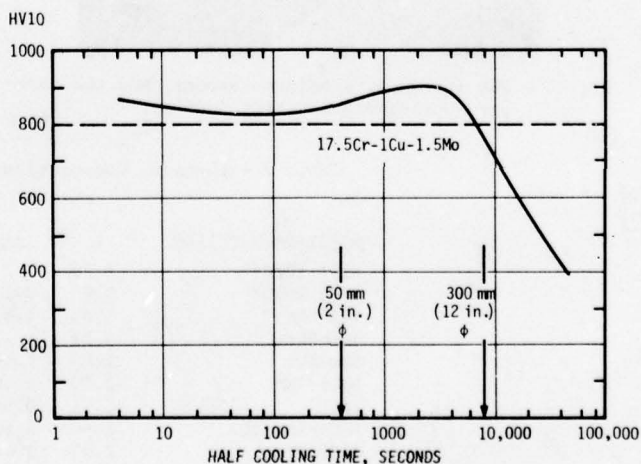


Fig. 5 - Hardness versus half-cooling time for a white iron containing 2.9% C, 0.8% Mn, 17.5% Cr, 1% Cu and 1.5% Mo austenitized at 955 C (1750 F) and cooled at various rates

It is evident that the iron containing 1% Cu and 1.5% Mo probably will not quite achieve the desired hardness in a section equivalent to a 300 mm diameter, and there are many mill components of that section size or larger. The reference provides several alloy combinations that will exhibit more than 800 HV to at least 8000 seconds half-cooling time. These irons contain the same base composition of 2.9% C, 0.75% Mn, 17.5% Cr and either:

2.9% Mo or
0.6% Ni + 1.4% Mo or
1.1% Ni + 1.4% Mo

Irons with higher nickel contents do not achieve the 800 HV hardness at all lower values of half-cooling time, so that in portions of a casting with faster cooling rates they will not exhibit the desired hardness. This is also the case with irons containing 1.5 or 3% Mn and 1.5% Mo.

The same irons were studied in the as-cast condition to define the alloy content required to suppress pearlite or other high temperature transformation constituents in various cast sections (7). Each iron was cast as a 30 mm dia bar, a 25 mm thick Y-block, a 50 mm thick Y-block, and a second 50 mm thick Y-block which was cooled to simulate the cooling rate of a 100 mm thick casting. Hardness and microstructure were determined on specimens from each cast section of each iron. For the purposes of this paper, it will suffice to tabulate the alloys which exhibited less than 5% high temperature transformation in the simulated 100 mm thick casting. The irons contained 2.9% C, 0.75% Mn, 17.5% Cr and either:

1.5% Mo + 1.0% Cu (or more) or
1.4% Mo + 0.6% Ni (or more) or
1.5% Mo + 3.1% Mn or
0.5% Mo + 2.1% Ni

All irons exhibited hardness in the range 550 to 597 HB.

TOUGHNESS AND ABRASION RESISTANCE IN HEAVY SECTION CAST STEELS - Many mining and milling applications involve severe enough conditions of repeated impact that white irons cannot be used. Some large grinding mills require combinations of white irons and steels. A 2.7 m diameter ball mill of the type shown in Figure 6, is an example of an ore grinding mill in which feed-end liners and feed-end shell liners can be constructed of heat treated Cr-Mo white iron, but discharge grates and discharge end shell liners must be constructed of cast steels of controlled toughness, to withstand the repeated impact of grinding balls as large as 85 mm diameter. The constant bed of ore in the feed-end cushions the liners from direct impact of the balls, but the discharge end can sometimes be depleted in ore, and the balls then impact the liners.

Some large grinding mills such as the 11 m diameter mill shown in Figure 7, depend on lumps of ore to serve as the grinding medium. These autogenous mills do not encounter as severe impact conditions, and white irons can serve as liners. Comparative wear rates of three liner materials are given in Table 4 for a different large mill, and demonstrate the improvement obtained with high Cr-Mo iron when it can be used.

When 125 mm diameter steel balls are added to increase throughput in large mills, the impact conditions are severe, and steel liners are required. The heavy liners in these "semi-autogenous" mills are made from tempered martensitic steels, with hardness in the range 350 to 400 HB. Because of the desire to improve liner life in these large mills, programs are in progress at this time to compare, in laboratory and field tests, various candidate steels including the pearlite Cr-Mo steels, austenitic 6Mn-1Mo steels, austenitic 6Mn-1Mo steels, and martensitic Cr-Mo and and martensitic Cr-Mo and Ni-Cr-Mo steels.

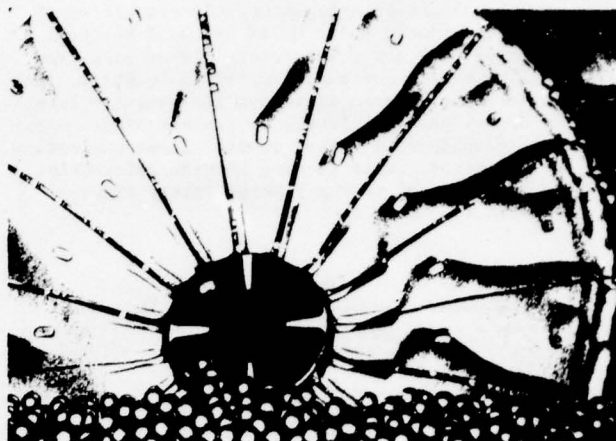


Fig. 6 - Interior of 2.7 m (9 ft) diameter ball mill

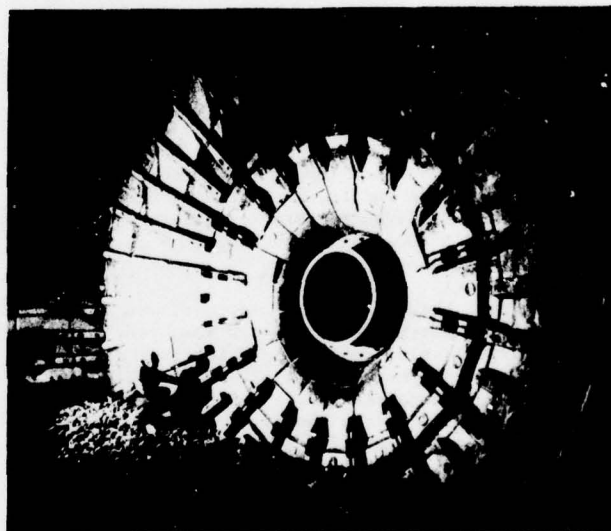


Fig. 7 - Interior of 11 m (36 ft) diameter autogenous grinding mill

Table 4 - Wear Rates of Lifter Bars in Autogenous Mills Grinding Taconite*

Material	Wear Rate	
	Lb/Ton Ore	kg/Mg Ore
Oil-quenched and tempered martensitic steel (0.4% C)	0.380	0.190
Pearlitic Cr-Mo steel (0.9% C)	0.550	0.275
Alloy white iron (15% Cr-3% Mo)	0.254	0.127

*Mill diameter = 8.2 m (27 ft)
Mill power = 4265 kW (5720 hp)

In one current investigation, the properties of commercially produced 0.45% C, 2% Cr, 0.5% Mo steel were compared with heavy laboratory plates cast from 3% Cr, 1% Mo steels containing 0.35% and 0.45% C. The objective of the program is to provide adequate toughness at higher hardness levels to improve liner life. The final results will depend on mill liner evaluation, but the laboratory tests to date provide interesting clues. A summary of Charpy V-Notch energy results is presented in Figure 8.

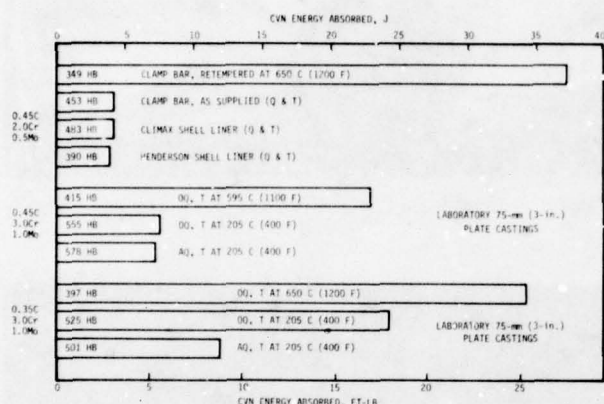


Fig. 8 - Charpy V-notch impact energy absorbed in specimens cut from commercial and laboratory castings of three candidate mill liner steels (OQ = oil quenched, AQ = air quenched, T = tempered)

It was evident that commercial castings, which are performing without breakage, do not have very high impact energy levels; apparently a level of about 4J is adequate at hardness levels of 390 to 480 HB. Presumably higher toughness levels may be required to resist fracture at higher hardness levels. The results indicate that considerably higher toughness can be achieved at hardness over 500 HB with the 0.35% C, 3% Cr, 1% Mo steel. Such a steel is expected to provide a considerable increase in liner life and be even more cost-effective than the current liners.

CONCLUDING REMARKS

At the risk of over-simplification, a few examples of the influence of alternate alloys in metal-to-metal wear applications and in abrasive wear applications were selected to address the "Alloy Question". The author believes, that for many wear applications involving large quantities of alloys, enough is known about the metallurgical characteristics required for acceptable performance so that adequate substitutions may be made for current alloys. Up until quite recent times, the incentive for alternate materials has been based almost entirely on operating efficiency and cost-effectiveness. In the last decade, the need to face shortages of energy and materials has added new incentives to the quest for alternate materials. But the needs must be put in proper perspective. Are the shortages short-range or long-range? Do they result from political motivation, changing technology, temporary limitations in production or gradually depleted reserves? Let us examine a few materials and processes which were discussed in this paper because of their technical contribution to wear resistance.

CASE HARDENING - New carburizing techniques are being developed to reduce the time and energy required to produce an adequate carburized case. Most involve

higher temperatures (for faster diffusion) and more sophisticated furnaces and instrumentation. The development is long-range and there will be time to test new materials for compatibility with the new processing techniques if they prove to meet the goal of reduced energy and cost effectiveness.

HEAT-TREATMENT - Periodic and geographic shortages of natural gas initiated efforts to eliminate gas furnace heat treatments. In this author's view, the supply of natural gas will be met with the development of pipelines from huge arctic resources, so that heat treatment should be eliminated only on the basis of total cost-effectiveness of the component being produced. One example is white cast iron for massive or complex sections. Elimination of high temperature heat treatment can reduce breakage and distortion, and alloy modification plus subcritical heat treatments can result in abrasive wear resistance almost as good as in the component given a full heat treatment.

COBALT - This alloy is an example of one which will be controlled by world-market pricing and politically motivated shortages on a continuing basis. The United States imports virtually all of its cobalt supplies. There is no doubt that cobalt will be available, but its future price may be somewhat unpredictable. This situation justifies the continued development of nickel-based and iron-based alternates. Such alternates may not be as versatile as the cobalt-based systems they are designed to replace, but the long-range need for the alternates is evident.

CHROMIUM - This alloy falls into the same category as cobalt; essentially all chromium supplies are imported. At this time, however, chromium is readily available. The Materials Advisory Board of the National Academy of Sciences has recently issued a comprehensive report which recommends continued search for alternates to chromium, so that any future disruption in supply could be managed by reserving available chromium for the most critical applications. In wear-resistant alloys, alternates are either less effective or more costly, but are available.

MOLYBDENUM - This alloy, which is mined principally in North America, is temporarily in tight supply because of strong demand world-wide. Primary molybdenum production has increased significantly in the last three years; however, production of by-product molybdenum from the copper industry has not increased. In fact, 1978 by-product molybdenum production was 5 million pounds less in 1978 than in 1977, while 1978 primary molybdenum production increased 16 million pounds over the 1977 level. Improved demand for copper in the last few months should result in increased production of by-product molybdenum. Production from the AMAX Henderson Mine reached 32 million pounds in 1978, and is expected to reach its capacity of 50 million pounds per year in 1980. AMAX has also announced that its Kitsault property in western Canada is expected to add 9 to 10 million pounds annually beginning in 1982. In addition, primary molybdenum producers, including AMAX, are expected to bring in new mines at known deposits in the U.S. and Canada. New sources will require substantial investments in time and money, but these investments will be necessary to satisfy the growing demand for molybdenum. Because of the long-range stability of molybdenum supplies especially with regard to domestic sources, there does not appear to be a need to develop alternate materials which do not perform as well. Efforts to optimize the molybdenum content in wear-resistant alloys will continue, with the objective of maintaining or improving cost-effective performance.

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WEAR IN ENERGY CONVERSION SYSTEMS

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ABSTRACT

In the search for new energy conversion systems to replace those dependent on short supply fuels, serious problems in wear control have been encountered. The most severe problems are found in coal gasification systems where high temperature erosion from high velocity hard particles chews up valves and elbows at an alarming rate and abrasion of coal handling and refining equipment indicates possible maintenance problems in full scale plants. Future transport of coal may require coal slurry pipelines. Erosion problems in slurry pipeline systems present as yet unsolved materials selection problems. Upgraded conventional coal-fired power generators present potential fly ash erosion problems.

Fretting-type wear in water cooled nuclear reactors is a continuing problem caused by heat exchange tubes and fuel rod vibration from flowing coolant.

BACKGROUND

The steady growth in the use of energy in this country has not only plunged us into a shortfall problem in fuel, but has also considerably strained the energy conversion systems to the point where breakdowns and failures have produced significant dislocations in energy use. Wear is a significant contributor to the problem. Although wear is not as spectacular a failure mechanism as fracture, it is just as crippling to a machine and often is more difficult to prevent.

Two types of wear cause the most trouble in energy systems: abrasive wear and erosion. Serious abrasive wear is usually associated with solid fuel processing equipment while erosion is a serious problem in the development of high technology energy conversion systems, such as advanced coal gasification plants. In a study by the National Academy of Sciences, it concluded in 1977 that, "The design decisions which must be made to have an energy conversion plant operate for more than 20,000 hours without a major and costly shutdown due to the failure of a critical component are not possible at the present time."⁽¹⁾ The component failure referred to has a high probability of being erosion or erosion-corrosion related.

Most notable among energy conversion systems in which significant wear problems are present are coal systems, nuclear power plants, and trash-burning power plants.

COAL SYSTEMS - Coal is abrasive because of its mineral content. Aluminum oxide and silica are two abrasive constituents found in coal in varying amounts. Western coals are much more abrasive than Mid-western or Eastern coal. Therefore, materials which may work well in the East may deteriorate rapidly when exposed to erosion or abrasion conditions with coal from Wyoming. It is important to distinguish between abrasive wear and erosion because the processes are different enough to require quite different approaches in wear control. Abrasion involves trapping particles between two surfaces and by moving one surface relative to the other causing the particles to cut and gouge the surfaces. Usually, the particles imbed in the moving surface and scratch or cut the stationary surface in contact. Loose particles will roll between the surfaces and produce rows of indentations or short scratch marks. Erosion involves impact of particles carried in a moving fluid or gas against a surface. The impacts cause indentation or cutting depending on the angle of impingement and particle velocity. Abrasion resistance is roughly a function of the ratio between the hardness of the surface and the hardness of the abrasive particles. The closer this ratio comes to unity, the greater the abrasion resistance. Erosion resistance is influenced by the velocity, size, and shape of the particles, the angle of impingement and the yield properties of the eroded surface. Hardness of the surface is not necessarily a guarantee of erosion resistance.

In coal fueled steam generators, the more serious abrasion problems occur in coal pulverizer equipment. Parts are made of Nihard, a nickel-chromium white cast iron.⁽²⁾ Since this material comes in several grades and structures, the best one for the abrasive conditions must be selected by trial. Parts that wear most rapidly are made to be replaced.

Erosion by coal occurs in feed pipes that deliver the powdered coal suspended in flowing air. Transport velocities are kept below 75-90 fpm and high enough to keep the coal flowing through bends and vertical rises. Erosion problems are the most severe in pipe bends where particle impingement occurs. Owing to the geometry of a pipe bend, the impingement angles change along the flow path from entrance to exit. The variation in impingement angle causes concentration of wear loss and rapid penetration of the pipe wall in localized areas. Experiments with air-blown sand have demonstrated this effect quite graphically.⁽³⁾ Worn pipe bend sections are shown in Figure 1 together with a diagram showing the location of the penetration of the elbow. Even though the pipe subjected to erosion by 230 μ m sand showed larger total weight loss, the pipe eroded

* Numbers in parentheses designate References at end of paper.

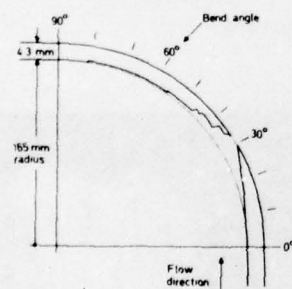
with 70 μm sand was more severely damaged owing to perforation. The erosion process is complex and depends on hardness, sharpness, size of particles, particle velocities, impact angles, and tendency of particles to follow flow lines or flow disturbances.



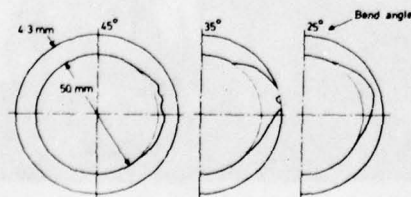
(a)

(b)

Bend wear photographs showing bends in which (a) 115 g was eroded by 230 μm sand at a phase density of 1.0 and a velocity of 32 ms^{-1} and (b) 44 g was eroded by 70 μm sand at a phase density of 3.0 and a velocity of 26 ms^{-1} .



(c) The outer bend wall wear profile of a bend that was eroded by 70 μm sand at a phase density of 3.0 and a velocity of 26 ms^{-1} .



(d) Pipe section profiles at various bend angles for the bend shown in Fig. 1(a).

Fig. 1. - Results of Sand Erosion Experiments in Pipe Bends (from Mills & Mason(3))

Fly ash from coal combustion is much more erosive than coal since it is concentrated mineral products from the coal. The fly ash can cause erosion problems in fluidized bed coal-burning furnaces, economizer baffles, draft fans, and cyclone separators. In some cases, ceramic wear plates are the only solution to severe fly ash erosion.

Transportation of the coal by slurry pipelines is a possibility for the future. If more coal is substituted for scarce oil and gas and large coal gasification and liquification plants are operated, the volume of coal transported from the mines will increase sharply over current experience. One way to move large amounts of coal long distances without traffic control problems is by mixing powdered coal in water in a slurry and pumping it through pipelines. Aside from the very difficult problem of water rights involved in Western states, there are very serious potential erosion problems. Current experience at the Black Mesa/Arizona slurry pipeline (18 inch, 5 million tons/year) has shown that pipe erosion problems are minimal if flow velocities are maintained at levels just high enough to keep the coal in suspension. The minimum settling velocity depends on the particle size distribution and the density of the design slurry. Velocities are currently maintained at about 5 fps. Considering pipelines projected for the future where throughputs will be ten times the Black Mesa experience, flow rates may have to increase to levels where pipe erosion will become a real problem. Design of pipelines will be difficult because of the unpredictability of erosion rates. Turbulent flow in slurries can cause localized substantial velocity increases with undetermined acceleration in erosion.(4) Erosion damage is most sensitive to velocity. Erosion rate is an exponential function of velocity and the exponent can go as high as 4 for some brittle materials. In addition to pipe erosion, the slurry preparation equipment is subject to severe erosion problems. Pumps, valves, and centrifugal water separators are the most vulnerable components. An example of an eroded pump casing from a coal slurry pipeline is shown in Figure 2. Recently, tungsten carbide (K-703) has been used successfully to combat erosion in coal-oil slurry pumps.(5) Hard facings for pump service have included Stellite 6 and plasma-sprayed tungsten carbide. The best performer has been borided steel.

Coal gasification and coal liquification processes present some of the most severe erosion problems ever encountered. The severity of the problem comes from high temperature as well as high velocities involving erosive fly ash and char from coal. Gasifier vessels, flow lines, valves, and solids removal equipment are all subject to difficult erosion problems. The National Academy of Sciences study has reported, "In advanced gasification concepts, operational experience is limited to pilot plant operation with operation periods of not more than 200 hours. This is insufficient experience to uncover erosion problems which may be serious enough in full-scale commercial operation to shut down the system."(1)

In coal liquification systems, valving is a particularly vulnerable component to erosion. High differential pressures result in high flow velocities through the valve during opening. The liquid is at high temperature and contains entrained hard particles from coal decomposition. Materials like Stellite 6 can be eroded in a matter of days. The hardest carbide and boride coatings (including advanced coating techniques) are being investigated for this severe service. Valve design is also being reconsidered to change impingement angles and reduce flow velocities.

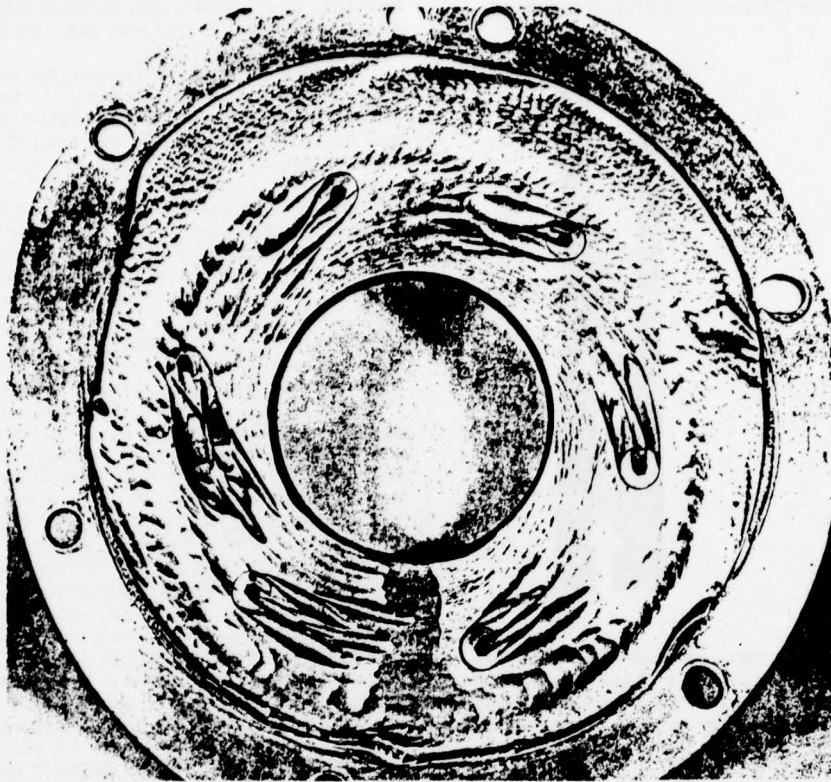


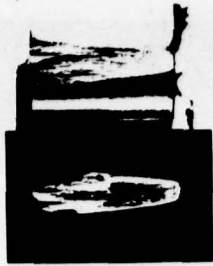
Fig. 2. - Erosion of Stainless Steel Pump Casting
by Coal Slurry

FRETTING WEAR IN NUCLEAR POWER GENERATORS - Water cooled reactors are subject to a fretting type wear involving zirconium alloy fuel rods and Inconel 600 steam generator tubing. Fretting is a type of wear resulting from contacting surfaces in very small amplitude oscillatory rubbing motion. The rubbing process produces a localized scar and releases debris which remains trapped between the surfaces and which acts as an abrasive medium. The result is wear of components that are not intended to wear. Fretting in reactors results from fuel rods and steam generator tube vibration caused by high velocity flow of heat transfer fluids. Owing to the temperature ranges seen by long fuel rods and steam generator tubes, they must be supported in a way to allow for thermal expansion. Therefore, spacers and tube sheets that separate the elements must position the rods and tubes, but allow axial movement. The rods and tubes rub and impact against the gliding surfaces producing classic fretting conditions. An example of a fretted zirconium alloy fuel rod is shown in Figure 3. Severe fretting from a test on zircaloy in 550 F water is shown in Figure 4. Once the conditions for fretting exist, there is little that can be done to prevent damage. Materials can be selected to reduce the effect and increase life, but the fretting cannot be eliminated. As a consequence, fretting has been a persistent problem in water cooled reactors since water cooled reactors were first built for electric power generation.



10X

Fig. 3. - Incipient Fretting on a Zirconium
Alloy Fuel Rod



2X

Fig. 4. - Fretting Damage on Zircaloy Alloy Specimens Tested under Simulated Reactor Operating Conditions in 550 F Water

Fretting in steam generators and heat exchangers from flow induced tube vibration is prevalent. In the newer designs for power plants, flow velocities are high and flow induced vibration has become a growing problem. Where carbon steel tube sheets are used, the fretting debris oxidizes and fills the clearance between the tube and the support channel immobilizing the tube and sometimes causing pinching of the tube, restricting the flow of fluid through the tube. Research has shown that increasing tube clearance with resulting impact loading increases the fretting wear rate.⁽⁶⁾ Use of alternative materials such as Incoloy 800 and Monel 400 has not significantly altered the fretting damage trends.

In nuclear power reactors, material selection is limited by corrosion constraints and neutron absorption properties. Therefore, fuel rod cladding has been limited to zirconium alloys. Trials with other materials (tantalum and niobium) have shown little improvement. However, recent experiments with sputtered platinum on Zircaloy have shown exceptional resistance to fretting in high temperature water.⁽⁷⁾

CONCLUSIONS

Wear problems (especially high temperature erosion) are slowing the development of coal conversion systems and causing significant loss of continuous power generation in large coal-fired and nuclear power generators because of down time for repair. The progress in solving these problems is slow because of the lack of understanding of the behavior of structural materials under conditions of erosion, abrasion, and fretting. Selection of a better material is not possible because engineers do not know of materials that are unquestionably "better" under high temperature erosion or fretting in 550 F water. Testing of materials under these conditions has produced a body of data containing conflicting results and wide scatter in wear rates for the same materials. It is because we do not understand the mechanisms that cause surface damage and release of debris during erosion and fretting that we cannot design proper test methods to obtain design information.

These problems have not been widespread in the past and, therefore, little attention has been paid to them in the engineering field. Rule of thumb or "common sense" methods used to solve these problems often result in no improvement or in worsening the situation. For instance, there is a need to test materials for coal gasification plants under anticipated high temperature erosion-corrosion conditions. From a practical and economic standpoint, these tests must be accelerated in time since the real system must operate for at least 10,000 hours. Erosion-corrosion can be

can be accelerated by increasing particle velocity, increasing temperature, or increasing total particle concentration. The use of any of these factors, however, can change the surface damage mode and produce misleading results. Just a change in the structure of scale growing on an alloy surface by an increase in temperature can make an order of magnitude change in erosion rate owing to the change in brittle behavior under particle impact. A change in yield properties or fracture toughness of an alloy at elevated temperature can significantly influence the way in which erosion progresses or the sensitivity to angle of impingement. At this point, there are no reliable methods which allow engineers to predict the effect of and interaction of operating parameters on erosion.

Research into the mechanisms of various wear processes is being carried out. Some progress is being made. However, if we want to solve our energy problems, both short and long term, much more research than is currently being done is needed.

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WEAR OF DENTAL TISSUES AND RESTORATIVE MATERIALS*

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ABSTRACT

A description of the clinical wear of tooth structure and restorative materials will be presented as well as a review of experimental methodology for studying wear of dental materials. Wear may result from physiological or pathological conditions. Mechanisms of wear often are influenced by both chemical and mechanical factors. Wear has been studied by service or clinical testing, simulated service measurements, model systems using wear instruments, accelerated aging, measurement of surface failure caused by single-pass sliding, and measurement of other properties.

CLINICAL WEAR OF TOOTH STRUCTURE AND RESTORATIONS

Wear of dental tissues may result from physiological or pathological conditions (1)**. The wear resulting from normal masticatory function is a physiologic process termed dental attrition. Bruxism and xerostomia are the most frequently reported pathological causes of wear. Wear also results from the abrasive action of instruments used by the dentist to finish restorations or to clean or polish the teeth. Dentifrices used by the patient with toothbrushing to remove undesirable surface deposits is an additional cause for wear of dental tissues.

Restorative materials in the mouth are affected by wear processes (2). Wear may be noticeable as the slight loss of marginal contour of an anterior restoration (Fig. 1) or severe as seen when gold restorations oppose porcelain denture teeth. Some restorative materials, such as porcelain and chromium-cobalt alloys may cause wear of opposing natural dentition. Excessive wear rates can lead to failure of an appliance and bring harm to supporting structures.

DENTAL ATTRITION - Normal masticatory function is accompanied by the wear of occlusal and interproximal surfaces of teeth (Fig. 2). Attrition is caused by function of the teeth (3) and is more severe in primitive than modern populations because of the nature of the aboriginal diet (tough meat and sandy, fibrous plants) and the use of the teeth for purposes other

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**Numbers in parentheses designate References at end of paper.



Fig. 1. - Wear of a composite restoration in an anterior tooth (Courtesy of J.B. Dennison, University of Michigan, School of Dentistry)



Fig. 2. - Severe occlusal wear caused by dental attrition (Courtesy of R.E. Buchholz, University of Michigan, School of Dentistry, From J.M. Powers and A. Koran, Mich. Dent. A.J., 55:119-126, 1973)

than eating. Attrition normally is compensated for by eruption of the teeth (4). When the rate of wear is faster than compensatory eruption, changes in vertical dimension and occlusion can contribute to pathologic conditions of the teeth and supporting structures. In modern populations, caries and periodontal disease

have replaced attrition as the causes of tooth loss (5). In areas where the opposing teeth do not contact, wear may be termed erosion.

The attrition of teeth in sheep has been studied for commercial reasons. Wear of the incisors of grazing sheep in New Zealand was more rapid on improved pasture than on unimproved pasture (6). It was suggested that chemical weakening of the teeth accelerated wear on the improved pasture. A correlation between degree of wear and amount of soil ingested by sheep has been observed (7).

BRUXISM AND XEROSTOMIA - Bruxism is a nonfunctional mandibular movement that is characterized by occasional or habitual grinding, clenching or clicking of the teeth (8). Little harm may result from mild bruxism; however, in severe bruxism tooth wear (Fig. 3) and alveolar bone loss can occur. In anterior teeth



Fig. 3. - Occlusal wear caused by bruxism (Courtesy R.E. Buchholz, University of Michigan, School of Dentistry, From J.M. Powers and A. Koran, Mich. Dent. A. J., 55:119-126, 1973)

incisal edges become flattened and polished, whereas small, saucer-like excavations appear in posterior teeth.

Xerostomia (dryness of the oral cavity) is caused by dysfunction of the salivary glands and can result in rapid destruction of enamel (9). In white rats, ligation of the major salivary gland ducts increased both tooth and periodontal bone loss (10). A high incidence of xerostomia is found in women during or after the menopause (11) and in patients receiving radiation therapy to the head and neck.

Less common forms of pathologic wear occur in people who are exposed to an unusual or severe environment. Examples are workers employed in silica refining plants or in sulfuric acid plants.

DENTAL ABRASIVES - Finishing and polishing techniques used in dentistry are meant to remove excess material and to smooth roughened surfaces often in conjunction with restorative procedures (12). Cleansing techniques are meant to remove food and other debris from a tooth surface without damaging it. The materials used for finishing, polishing and cleansing are primarily abrasives and are applied by means of

numerous dental tools or as slurries or pastes. Finishing and polishing of restorative dental materials are important steps in the fabrication of clinically successful restorations. Polishing and cleaning are routine procedures for maintaining the health of the dentition. These procedures, however, can lead to roughened enamel surfaces by the use of excessively abrasive materials. Prophylactic pastes and dentifrices will be discussed here.

Prophylactic Pastes - A dental prophylactic paste should be sufficiently abrasive to remove effectively exogenous stains, pellicle, materia alba, and oral debris from the tooth surface without imparting undue abrasion to the enamel, dentin or cementum. Products containing mostly quartz and pumice show higher cleansing values but generally result in greater abrasion to enamel and dentin (13). Abrasion of dentin by a pumice slurry has been measured to be about 20 times greater than abrasion of enamel under standardized conditions (14). A proposed American Dental Association Specification No. 37 for Dental Abrasive Powders may require that the abrasiveness of a powder be stated.

During a prophylactic procedure, care must be exercised to avoid excessive abrasion of any restorative materials present. Polymeric materials, such as denture base and artificial tooth resins, composite restorations and pit and fissure sealants are particularly susceptible to wear because of their low hardness (12). The undesirable results of such wear can be reduction in anatomic contours and increased surface roughness.

Dentifrices - The primary function of a dentifrice is to clean and polish the surfaces of teeth accessible to a toothbrush (12). The abrasives found in dentifrices include calcium carbonate, dibasic calcium phosphate dihydrate, anhydrous dibasic calcium phosphate, tricalcium phosphate, calcium sulfate, calcium pyrophosphate, insoluble sodium metaphosphate, and hydrated alumina. These are primarily cleansing and polishing abrasives that are not intended to abrade enamel. In 1970 the Council on Dental Therapeutics of the American Dental Association reported an abrasivity ranking of commercial dentifrices compared to a standard abrasive for dentin (15). Abrasion of enamel by modern dentifrices is not considered a problem unless unusual oral conditions exist; however, exposed dentin and cementum are susceptible to wear if improper brushing techniques are used (Fig. 4). The bristles of the toothbrush itself have little abrasive power, although they do influence the abrasion caused by the dentifrice.

Polymeric restorative materials are susceptible to abrasion from toothbrush and dentifrice use. Dentifrices should not be used in the routine cleaning of denture bases or acrylic denture teeth.

MEASUREMENT OF WEAR

Wear has been studied by clinical testing, simulated service testing, model systems using wear instruments, accelerated aging, measurement of surface failure caused by single-pass sliding, and measurement of other properties (16). It would be desirable to have an *in vitro* test to predict the amount of wear observed *in vivo*, but such correlation probably is not possible. It is more reasonable to attempt to rank materials in the same order with clinical observations, but also it is important to study mechanisms of wear to improve wear resistance.

CLINICAL TESTING - The clinical testing of restorative materials in humans gives reasonable assurance that the combination of parameters affecting wear in the test group will be similar to those in the total population. The disadvantages of clinical studies include the time and effort involved, the difficulty of interpreting mechanisms of wear, and the

difficulty of quantifying the wear.

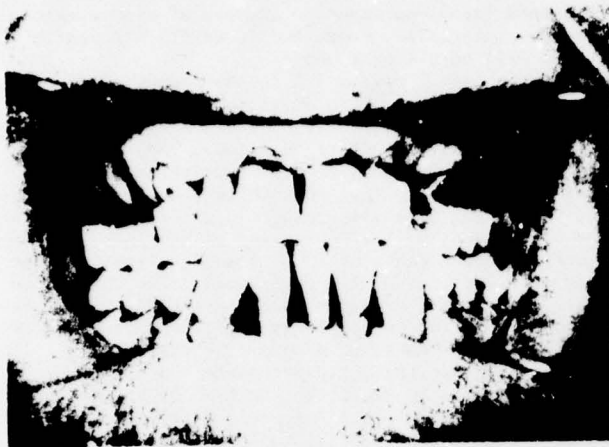


Fig. 4. - Cervical abrasion from improper use of toothbrush and dentifrice (Courtesy of R.E. Buchholz, University of Michigan, School of Dentistry, From J.M. Powers and A. Koran, Mich. Dent. A. J., 55:119-126, 1973)

The clinical comparison of the wear of composite and amalgam posterior restorations involves evaluation of parameters such as anatomic form and margin adaptation using the United States Public Health Service criteria (17). In one study 87 percent of the amalgam restorations retained their original anatomic form after two years, whereas only 47 percent of the composite restorations were rated as no change by trained clinicians (18). Impression techniques have been used to study mechanisms and rates of wear *in vivo* (19,20).

SIMULATED SERVICE TESTING - Numerous studies of the abrasive wear of teeth caused by dentifrices and prophylaxis materials have been reported. One method involves measuring the amount of tooth tissue abraded from an irradiated tooth by the concentration of radioactive phosphorus in the wear debris from brushing (15,21,22). A second method involves determining the change in the profile of samples of tooth structure during brushing (23).

The wear resistance of denture teeth has been studied by the use of sets of teeth opposing each other in a machine that simulates chewing (24). Less wear was observed for acrylic opposing porcelain teeth than acrylic opposing acrylic teeth using this machine.

WEAR INSTRUMENTS - A wide variety of wear instruments have been used to rank dental materials. Two of these wear tests are the two-body abrasion test (25,26) and the pin-on-disk test (27). One two-body abrasion test (25) utilizes a modified surface grinder to rub a cylindrical specimen on an abrasive (e.g. silicon carbide) paper. The rate of abrasion for glass-filled (A) and quartz-filled (B) commercial composite resins and some experimental modifications of them are shown in the Table. The rankings observed with the silicon carbide abrasive agree with rankings found with other abrasives such as alumina, garnet, quartz, and glass (28).

Table - Rate of Abrasion of Experimental Formulations and Commercial Composite Resins (25).

Material	Rate of Abrasion, $10^{-4} \text{ mm}^3/\text{mm of travel}$		
	Commercial Formulation	Resin with non-silanated filler	Resin without filler
A	7.73 (0.99)*	13.8 (1.5)	17.0 (1.1)
B	3.84 (0.20)	5.60 (0.20)	18.8 (0.6)

* Mean of 6 replications with standard deviations in parentheses.

The pin-on-disk test (27) utilizes a cylindrical sample of human enamel on porcelain to rub on a rotating disk of composite resin or amalgam. Measurements of wear rates are possible, but transfer of material from the disk to the pin confuses interpretation of the results.

ACCELERATED AGING - The surface degradation of composite resins caused by accelerated aging in a weathering chamber has been studied (29). Erosion of the resin matrices and exposure of filler particles were observed. After 900 hours of aging, differences in surface roughness and profile suggested that the resins were eroded at different rates. Surface crazing was observed for some resins. Accelerated aging holds promise as a model to simulate the erosive wear of composite resins.

SINGLE-PASS SLIDING TEST - The mechanism of wear during sliding can be studied when a single sliding track is examined (30-32). The track is formed by allowing a diamond hemisphere (360 μm in diameter) to traverse a flat specimen at various normal loads. Parameters such as track width, tangential force and mode of surface failure can be measured. Three modes of surface failure observed for single crystals of fluorapatite under sliding are shown in Fig. 5.

DUCTILE TO BRITTLE TRANSITION on
basal plane of fluorapatite single crystals



Fig. 5. - Ductile, tensile and chevron modes of surface failure of fluorapatite under sliding.

Single-pass sliding has been used to study a number of dental materials including dental amalgam, composite

resin, human enamel, and feldspathic porcelain (16,33).

MEASUREMENT OF OTHER PROPERTIES - Numerous other mechanical properties such as hardness, tensile strength, elastic modulus, and fracture toughness have been measured to determine a relationship with wear. Findings indicate that values of tensile strength and hardness of composite resins are not related to measured abrasion rates (34). An equation has been proposed that relates abrasive wear to scratch width and modulus of elasticity in bending (35), but this model does not account for the effect of mode of surface failure on the wear process. Fracture toughness data were consistent with modes of surface failure of composite resins observed in single-pass sliding (36). The influence of zeta-potential on the wear of fluorapatite single crystals has been reported (37).

SUMMARY

Wear of human teeth and restorative materials may result from physiological or pathological conditions. A variety of methods have been used to investigate these wear processes. It is important not only to evaluate data from laboratory simulations and clinical tests, but also to study the nature of the wear process by tests such as single-pass sliding and accelerated aging.

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WEAR IN MATERIAL PROCESSING

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ABSTRACT

The consequences of wear problems for productivity in material processing are reviewed. In particular wear in machining, rolling, molding, and dust collection processes is discussed. Specific examples are cited to provide information on actual operating experiences. Data are provided on solutions to wear problems and on the resulting increase in process efficiency. The information provided shows that significant increases in productivity can be obtained by implementing either alternate materials or coatings to reduce wear. There is no general approach to solving wear problems; each must be evaluated in terms of the specific cause of the excessive wear.

THE WEAR COMPONENTS IN PRODUCTION EQUIPMENT for material processing can have a profound effect on industrial productivity. The consequences of wear for productivity are manifested in machine downtime, cost of replacement parts, and the fabrication of products which do not meet specification. These factors all contribute to the cost of the product. Consequently the alleviation of wear problems will result in overall productivity improvement and reduce the effect of inflation.

The influence of wear in material processing is far reaching and touches on numerous processes in many industries. The purpose of this paper is not to survey the breadth of the problem, but to select and discuss some specific examples of the impact of wear on processing. In particular data are included for machining, rolling, molding, and dust collection operations. For each of these topics the discussion will include a description of the nature of the wear problem, the solutions attempted, and the impact of the solutions on productivity.

MACHINING

Improvement in the life of expendable cutting tools has been an active area for increasing process efficiency because of the magnitude of machining in the United States. There are many methods of improvement through alternate tool materials or tool treatments. One class of alternate material which has shown potential is that of extremely hard materials, namely, polycrystalline diamond and boron nitride. Polycrystalline diamond has been cited for reducing tool costs and machine downtime in the machining of silicon aluminum and babbitt bearing alloys for automotive applications (1).^{*} Tool blanks are prepared by growing diamond crystals together on a tungsten carbide substrate.

Details on the application of polycrystalline diamond to the machining of wrist pin bores in an aluminum piston are given in Table 1. The annual tool

savings in this case amounted to over \$6,000. Additional savings the amount of which has not been documented accrued because of greater throughput due to lower machine downtime for tool changes.

In another case the polycrystalline diamond was employed to machine a finish bore in a babbitt bearing. As in the previous case the competing tool was tungsten carbide. The results are summarized in Table 2. Annual tool savings of \$2,107 were derived from a 75 percent reduction in tool cost per piece. Another benefit was the reduction of machine idle time per month from 4.9 hours to 0.045 hours.

Boron nitride has been shown to provide much longer tool life relative to carbide tools in the machining of chilled cast iron, which has a hardness of about 61 Rc (2). Conditions and economics are presented in Table 3. In this case the good wearing characteristics of the boron nitride provided a high material removal rate, and a final grind was not required. Consequently, in addition to the benefits of increased tool life, throughput was increased significantly. The carbide tool suffered in comparison not only from more frequent changing but also because machine adjustments had to be made more frequently to compensate for wear.

ROLLING

The rolling of automotive friction materials to form linings is impacted by the wear of the rolls. The friction material is a composite consisting of reinforcing fibers and inorganic particles held together in a polymer matrix. This roll--a hollow cylinder located on a mandrel along with similar rolls--must rotate between two clamp rings located on the lower roll, which fixes the roll position and the width of the lining. Although the roll was lubricated with a mold release, edge wear and ultimately chipping were found to limit the life of the roll.

Originally the rolls were made from an SAE 8620 case-hardened steel. A solution to this wear problem was found when a through-hardened tool steel (Rc 58-62) was substituted for the case-hardened alloy. The life of the roll was increased to over 300 percent of its original value. Easier dimensional control during roll fabrication contributed additional benefits because the tool steel did not require a carburizing and normalizing heat treatment operation. When the tool steel roll did finally wear, it could be reground and reused. The case-hardened alloy steel roll had to be discarded or heat-treated again once the wear exceeded the case depth.

MOLDING

Die mold wear is generally the limiting wear factor in molding operations. In the manufacture of automotive friction materials in pad form the compaction of the mix is an important operation. Mold wear of up to

^{*}Numbers in parentheses designate References at end of paper.

Table 1 - Machining of Wrist Pin Bores in Aluminum Pistons (1)

Material Machined: Silicon Aluminum SAE 332,
Brinell 90-121
Machine Type: Fuller Transfer Line
Tool Material Replaced: Tungsten Carbide, C-3 Grade

<u>Machining Conditions</u>	<u>Tungsten Carbide</u>	<u>Polycrystalline Diamond</u>
Cut Depth	0.005 in.	0.005 in.
Cutting Speed	2909 SFPM	2909 SFPM
Feed/Revolution	0.005 in.	0.005 in.
<u>Economics</u>		
Tool Cost	X	16X
Pieces/Edge	383	100,000
Regrinds/Tool	4	3
Total Pieces/Tool	1915	400,000

Table 2 - Machine Finish Bore in Babbett Bearing (1)

<u>Machining Conditions</u>	<u>Tungsten Carbide</u>	<u>Polycrystalline Diamond</u>
Cut Depth	0.015-0.030 in.	0.015-0.030 in.
Cutting Speed	1292 SFPM	1292 SFPM
Feed/Revolution	0.002 in.	0.002 in.
<u>Economics</u>		
Tool Cost	X	23X
Cutting Edges/Tool	3	1
Pieces/Edge	475	61,000
Pieces/Tool	1425	61,000

Table 3 - Machining of Grey Cast Iron Mill Rolls (2)

<u>Machining Conditions</u>	<u>Carbide Tool, C-3</u>	<u>Boron Nitride Tool</u>
Cut Depth	0.125-0.180 in.	0.090-0.100 in.
Speed	45-50 SFPM	275-300 SFPM
Feed	0.020-0.030 IPM	0.012-0.020 IPM
Material Removal Rate	2.0 in ³ /min	4.8 in ³ /min
Turning Time/Roll	44.1 hours	37.5 hours*
Grinding Time/Roll	8 hours	not required
Total Machining Time/Roll	52.1 hours	37.5 hours
Relative Tool Life	X	4X

*Thirty-five (35) hour scale removal with carbide and 2-1/2 hour finish cut with boron nitride.

0.020 inch could be tolerated before rework or replacement was required.

A first approach to reducing mold wear (AISI-D2 steel) was chromium plating. However, spalling of the coating during service limited its life, and consequently no mold life increase was realized. A second approach which proved successful was the application of a hard proprietary plating (Poly-Ond). This coating had a hardness of about 60 Rc and provided a smooth antifriction surface. Life tests in production are still in progress, but to date the coated molds have already exceeded the life of the uncoated molds by 25 percent and the coating is still intact. An additional benefit is the elimination of sticking between the cold compact and tooling because of the smooth antifriction surface of the coating.

Another example where surface coatings have been used to increase mold life is in the compression molding of elastomers filled with crystalline boron particles (3). The abrasive action of the boron particles on the walls was found to limit mold life from 100 to only a dozen parts. The molds were made from either AISI H-13 or AISI A-6 steels hardened to Rc 40. Chromium plating was also tried in this application. However, the cost of reconditioning worn molds and the localized nature of the mold wear-out (which produced parts with imperfections) made this an unacceptable approach. The various coating methods attempted to alleviate this wear problem and the relative effectiveness of each are presented in Table 4. Although a number of coatings provided increased life over the

Table 4 - Relative Durability of Various Wear-Resistant Coatings Tested (3)

Coating (Method of Application)	Thickness (μm)	Run-In	Steady State
TiB ₂ (CVD)	3.8-8.6	19	130
Al ₂ O ₃ /Cr ₃ C ₂ (CVD)	-	4.2	5.2
W/W ₂ C (CVD)	6.7-38.6	3.0	4.8
Hard Chrome (Electroplate)	-	3.5	4.0
Al ₂ O ₃ (CVD)	3.8-7.5	5.1	3.5
Nickel/Diamond (Electroless Ni Plate)	50	3.9	3.2
A-6 Steel (reference)	0	1.0	1.0
Cr ₂ O ₃ (Plasma Spray)	48	0.9	1.0
Al ₂ O ₃ + TiO ₂ (Plasma Spray)	66	0.74	-

reference uncoated A-6 steel, the TiB₂ was by far the most effective and was selected for production use.

Further studies on process economics indicated that sputtering was a more cost-effective process than chemical vapor deposition. Consequently a sputtered TiB₂ coating was evaluated. A 5 μm sputtered coating was found to provide even greater durability with a relative value of 24 for run-in and 650 for steady state. The sputtering process was therefore accepted for production use.

DUST COLLECTION

Often a process which is not applied directly to the product is forgotten when improving production efficiency. However, all such processes must be considered, since they are necessary and included in the production cost for the product. One such example is the air treatment operation used to remove dust (including abrasives) following a grinding operation for automotive friction materials.

A cyclone-type dust collector made of abrasion-resistant steel was found to wear paper thin after two years of operation. Attempts were made to improve this by lining the collector with a cement-type material. This did not prove efficient because patching of the cement coating was required on an annual basis. A second approach with rubber-based coating (Linatex Corp.) was found to be successful. A dust collector with this coating has been in operation for three years, and no significant coating degradation has occurred.

CONCLUSION

The cases cited in this paper show that significant increases in productivity can be achieved by reducing the wear encountered in widely varying processes. Gains were realized in the life cycle of expendable tools, rolls, molds, and dust collectors. In each of these cases the solution to the wear problem was different. This highlights the fact that wear impacts many different processes and the solutions are as varied as the processes themselves. Each wear problem must be considered not only in light of the particular process, but also in light of the particular environment and operating conditions for that process.

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MEASUREMENTS AND STANDARDS FOR DRY WEAR

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ABSTRACT

The needs for improved capability in accurately determining the wear rates of materials will be discussed. Activities currently underway to develop and provide reference materials for wear testing, to improve wear measurement procedures and to obtain meaningful wear data will be described. A comparison will be attempted in the current state-of-the-art between wear and corrosion.

PROGRESS IN MATERIALS research and development in recent years has been evident in many areas of technology. For example, improved performance and durability in current gas turbine engines is due primarily to new and better materials of construction. In the area of lubricated systems such as rolling contact bearings, improved metallurgical processing to reduce non-metallic inclusion effects has significantly extended the fatigue lives and hence the bearing design lives. Dry wear situations have themselves been favorably impacted by materials R&D. This can be seen most easily, perhaps, in connection with metallic (and non-metallic) hard coatings that provide considerably better abrasive wear resistance and lifetimes in service.

It is important to note, however, whether advances such as these and others in providing more durable, higher performance materials have resulted from an improved understanding and application of fundamental materials science or whether only empirical and incremental progress is involved. In the area of dry wear of materials it is believed that the latter situation exists and that only recently has any significant research effort been mounted in the U.S. to change this situation. In this paper a brief discussion will be presented to indicate some of the barriers that oppose further advances in the development of wear resistant materials and an improved understanding of dry wear. The scope of this paper will be limited to dry wear of metals since other papers in the symposium will be addressing other areas of lubrication and wear. It is also interesting to compare the field of corrosion research and engineering with wear research and engineering; a few interesting connections will be attempted concerning measurement capability and standards in the two fields.

APPLICATIONS CONCERNED WITH DRY WEAR PROCESSES

The most commonly experienced wear process in service (1*) is probably abrasive wear, caused when

* Numbers in parentheses designate References at end of paper.

hard, cutting particulates either gain access to a concentrated contact zone (e.g., a bearing) or abrade an exposed surface under some imposed load. Figure 1 shows an example of an abraded surface on a 0.2% carbon steel specimen. In many cases the wear conditions are lubricated rather than dry, however,

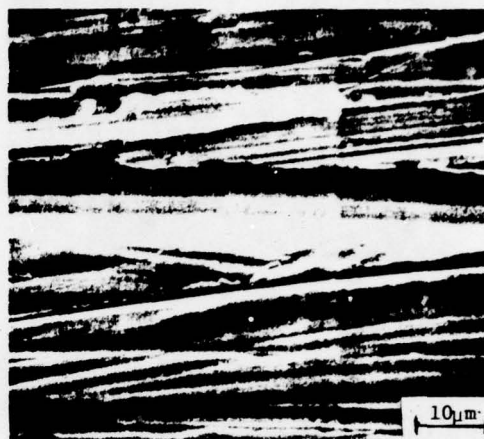


Fig. 1. - Abraded surface on 1015 steel using 50 μm Al_2O_3 (2 body) abrasive.

the abrasive particles are so much larger than the protective, lubricating film that abrasive-metal contact results and the lubricant has little beneficial influence. As examples of applications, we can consider mining equipment, construction equipment, industrial operations involving solids-handling, and many types of rotating machinery and systems.

In the absence of abrasive particles, metal-to-metal contact can occur under dry or inadequately lubricated conditions and also produce unacceptable wear rates. This wear mode is usually called adhesive wear and is frequently the result of a combination of processes such as plastic deformation, fatigue, surface and subsurface crack growth, and an adhesive or aggregating process that leads to the formation of large wear particles or transferred material between contacting surfaces. Applications include (2) sliding contacts such as dry gear surfaces, office equipment, and solid and oil-lubricated bearing contacts where lubricant failure has occurred.

Erosion due to solid particle impact (rather than fluid flow) can be a serious wear problem in certain industrial situations (3). Much attention has recently been paid to energy conversion systems such as coal gasifiers and fluid bed combustors, however, older industrial processes concerned with transfer of abrasive-gas mixtures have previously suffered from considerable erosive wear. One significant barrier to gas turbine use in combined cycle coal gasification systems is particulate erosion of turbine blades and components. An example of an eroded AISI type 310 stainless steel surface is shown in Fig. 2.

While not meant to be exhaustive, this discussion should convey to the reader some recognition of the broad scope of dry wear problems in current technology. Many other examples can be found in the references cited and in standard text books on the subject (4)(5). The amount of research and materials development directed toward dry wear problems so far is not believed to have been commensurate with the incidence of those problems. Many authors at recent conferences (6) have pointed out the lack of an adequate foundation of

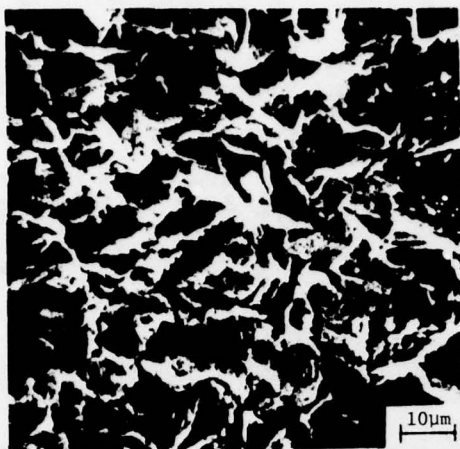


Fig. 2. - Solid particle eroded surface on 1015 steel using 50 μm Al_2O_3 abrasive particles.

science from which to address these dry wear problems. Recognition of this need finally appears to have arrived, hence, one may expect the next few years to produce useful and far reaching developments.

MEASUREMENT PROBLEMS IN WEAR

Wear is a complex process that can include several different, simultaneous mechanisms. Mechanical processes such as plastic deformation, crack growth and fatigue are frequently present. Chemical processes such as surface oxidation, corrosion product formation, and environmentally assisted crack growth are also frequently involved. Therefore, the design of a proper laboratory test method that includes all relevant conditions of exposure and which gives reasonable correlation with service experience can be a formidable task. As an added difficulty it is well documented that wear measurements are notoriously difficult to reproduce at an adequate level. In this section a brief discussion of these two problems - test method adequacy and measurement precision - will be given.

A laboratory faced with a typical wear measurement problem must select the materials to be tested, a machine or test geometry, and the environment to be used. The materials choice is usually straightforward. The remaining two choices can be very difficult. Consider the choice of a test geometry. Assuming that a full scale simulation of the service conditions is not feasible, there must be a number of decisions made concerning size, load, speed, time, and contact shape details. An adequate understanding of the implications of choosing particular values is rarely achieved. For example, in reducing the contact size by a certain factor, does one also scale the local stress maximum or stress distribution, the surface temperature or subsurface temperature distribution, etc.? A recent collection of laboratory wear test systems (7) includes over 200 different designs! Generic similarities exist there, however, the effect of different size scales, loads and surface speeds are not known. In response to this difficult situation, the ASTM Committee G2 on Erosion and Wear held a conference on Wear Tests for Metals (8) in 1975. The proceedings of that conference provide a valuable source of information on evaluated test methods. Specific tests for dry sliding wear, abrasive wear and erosion are described in the articles contained therein. A second symposium concerned with polymeric materials was recently sponsored by the G2 Committee.

As one example of the capability for precise wear testing, consider the so-called dry sand/rubber wheel low stress abrasion test (9). That method is currently involved in a round-robin measurement series in ASTM-G2. A draft standard for this method has been developed and appropriate test machines are in use in more than 10 different laboratories. Results using this machine and method in our own laboratory and several others have shown that wear rate values can be determined within one laboratory to relative precisions of better than 5%. Interlaboratory comparisons without the use of any reference materials have approached agreement to within 10% to 20% in many rounds (however, widely different values do still occur in this case). While this process is not yet concluded, it is expected to lead to an established abrasive wear test method capable of precise measurement of material wear rates. Fig. 3 shows a wear scar resulting from this test

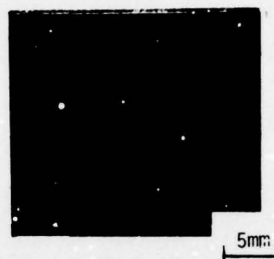


Fig. 3a. - Abrasive wear track on 1015 steel specimen using dry sand/rubber wheel test.

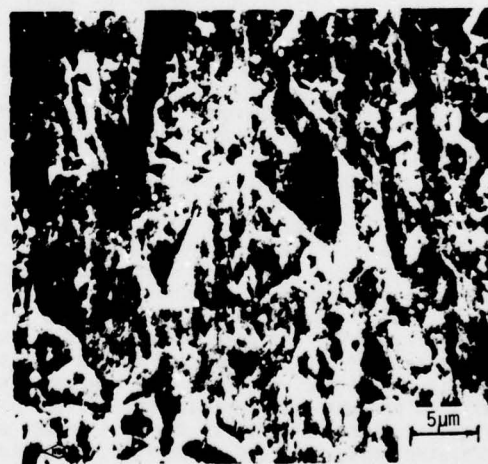


Fig. 3b. - Abraded surface on 1015 steel using 50 μm Al_2O_3 (3 body) abrasive.

geometry on a 0.2% carbon steel surface as well as a magnified view of the worn surface morphology. Another comparative measurement activity concerning dry wear that is underway involves solid particle erosion. To further establish a baseline of measurement in these two cases, the NBS plans to make available reference metal specimens for use with these ASTM standard methods of testing. While certified values of wear rates cannot be provided in these cases, it will be possible to assure the user of the homogeneity and traceability of the reference material as well as access to the body of comparative laboratory testing on the same metals. Test method standardization activities concerning lubricated contacts are also underway in the ASTM-D2 Committee.

The third consideration in wear measurement problems involves the test environment. It is of course possible to select a very reproducible laboratory environment, for example, dry nitrogen gas. However, results on the wear rates of metals under those conditions will not necessarily correlate with any actual service experience. Here the laboratory is faced with the problem of simulating the service exposure conditions in a way that also permits reproducible measurement conditions. If the chosen method already includes scaling of surface speed or load and hence surface temperature, then the appropriate environment may require scaling of the oxygen concentration or some other chemical activity. It is rarely possible to make such adjustments with any assurance of acceptable simulation of service experience. In fact the usual approach to this problem is to select some relevant but controllable environment and then obtain preliminary wear data on materials in order to make decisions on subsequent full scale wear testing programs. This approach may be the only feasible one until a much better understanding of wear fundamentals is achieved, including the effects of environments.

One important aspect of any discussion of wear measurement problems is the existence of evaluated data on wear rates of materials. Relatively few comprehensive sets of data are available on material wear rates. Reports from individual studies do contain wear rate data, however, the precise conditions of measurement usually are not given. Frequently text books (4) and other authoritative sources are reduced to quoting wear coefficients to the nearest order of magnitude in order to handle conflicting wear data. An obvious need exists for the development of reference measurement methods and the accumulation of accurate wear data on at least some common materials. More will be said on this point in connection with the comparison of corrosion and wear measurement capabilities.

Wear measurements can involve more than simply dimensional changes and determinations of weight losses. Wherever plastic deformation is important during wear, for example, the determination of mechanical stress patterns may be required for complete wear analysis. Studies bearing on the density and size of fatigue cracks near a wearing surface may be useful to determine the remaining life of a component. A relatively new approach to wear measurement concerns studies of wear debris particles recovered from wearing systems. In this method (10)(11) it is possible to sample a wearing system during operation and monitor the wear rate as well as the active modes of wear (Fig. 4). This approach permits in some cases an early

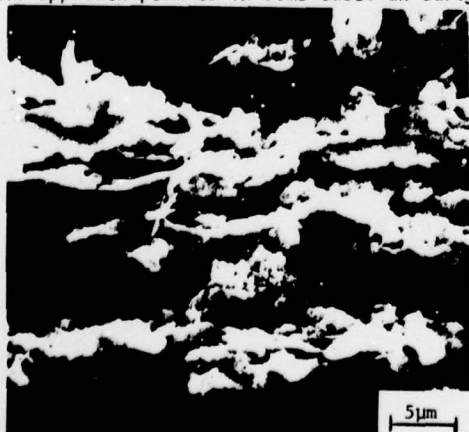


Fig. 4. - Wear debris recovered from an abraded 1015 steel surface (as in Fig. 1).

diagnosis of failure and can avoid unnecessary repair or maintenance operations. It has been suggested (12) the debris analysis also can be used in laboratory studies to indicate whether successful simulation of field wearing conditions has been achieved. In a diagnostic sense, wear debris analysis can be thought of as analogous to the recovery and analysis of the products of corrosion.

STANDARDIZATION ACTIVITIES

Proper methods for measuring the wear rates of different materials in the laboratory require appropriate standardization and calibration. Many laboratories with experience in wear measurements have their own internal standards and reference materials. In this way consistent measurements are assured on a given wear test system in that laboratory. Unfortunately experience has shown that following this scheme exclusively can lead to the introduction of systematic errors as well as unnecessarily large random errors in the measurement process. Comparative measurement exercises with other laboratories frequently reveals these built-in errors. There are of course many professional societies and voluntary standards groups that provide standardization support in physical and chemical measurements. Relatively little has been available so far, however, in the area of wear measurements. This situation is one of great concern to the ASTM Committee G2 and several activities are now underway in G2 to correct this situation. As indicated below the Committee is organized technically in three principal erosion and wear areas. Measurement methods development and round robin activities are underway in all three technical subcommittees. In the cavitation area both methods and data on a number of materials are now available. A solid particle erosion round robin is underway and a reference material is being selected.

ASTM Committee G2 Erosion and Wear

Chairman: G. F. Schmitt, Jr.
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F. J. Heymann
Sub 2.1: Erosion by Liquid Impact and Cavitation (F. G. Hammett)
Sub 2.2: Erosion by Solid Particle Impact (W. F. Adler)
Sub 2.3: Wear (K. Budinski)

The wear subcommittee is now finishing an extensive round robin (containing materials data) concerned with abrasive wear. Other standards are being developed in G2 as summarized below. It is believed that with proper industrial participation, this approach should produce a needed minimum number of

G2 Standards (April 1979)

G32-77 Vibratory Cavitation Erosion Test
G56-77 Determination of the Abrasiveness of Ink Impregnated Fabric Printer Ribbons
G40-77 Erosion and Wear Terminology and Definitions
(Draft) Dry Sand/Rubber Wheel Abrasion Test
(Draft) Solid Particle Erosion Test
(Draft) Jaw Crusher Gouging Abrasion Test
(Draft) Ring-on-Block Wear Test

standard dry wear test methods and materials in a few years. Active participation is sought in this work. (Note that available standards for lubricated wear measurements through Committee D2 include the four ball geometry, the Timkin (ring/block) geometry, and the Falex (pin/vee block) geometry).

COMPARISON: WEAR AND CORROSION

There are some interesting comparisons that can be made concerning the state of measurement science, fundamental understanding, and standardization between wear and corrosion. The purpose in making a few comments here will be to suggest that more effort is needed in the wear area if improvements in the wear durability of materials is to occur and if a deeper fundamental understanding is to develop.

Both wear and corrosion represent serious and costly degradation mechanisms. Both involve local, microscopic processes. There are overlapping areas that include mechanical effects on corrosion, for example stress corrosion, and strong chemical effects on wear, for example, fretting corrosion. In both cases it is the combined chemical/mechanical reactions that cause difficulty in obtaining useful measurement results and in successfully modeling the processes. Wear rates can vary by more than four orders of magnitude for changes in the environment.

A substantial amount of basic data as well as engineering information is available to assist the corrosion scientist. These include thermodynamic considerations of stable and unstable (corrosion) regions for many metal/environment systems. The National Association of Corrosion Engineers has led numerous activities to compile and disseminate corrosion information, for example, the Corrosion Data Survey. There is no single comparably sized professional society as active in the wear area where the response to such needs is more diffuse. A current activity of the American Society of Mechanical Engineers is to produce an extensive Wear Control Handbook that will fill an important need for design information and wear data on materials. Hopefully other needed activities concerned with wear fundamentals and wear information will develop soon.

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(Abstract and text were not provided for publication)

DIAGNOSTICS OF WEAR IN AERONAUTICAL SYSTEMS

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ABSTRACT

There is a strong economical motivation for monitoring the health of expensive or safety critical systems. This is particularly true for commercial and military aircraft where maintenance costs follow not too far behind fuel costs in overall operating expenses. Most of the operating costs are engine related for fixed wing aircraft. Diagnostic monitoring is a particularly strong thrust in the growing helicopter market. Here maintenance costs associated with the transmissions and drive train greatly increase the maintenance burden and failure risk. Detection measurements fall under two general categories of vibration and particle detectors. The latter are more amenable to tracking wear. There are presently many military programs evaluating diagnostic systems. Greater attention and documentation is now being given at overhaul to wear and failure modes. Some very useful studies have been conducted on the wear and failure modes of particular aircraft. Wear debris analysis can supply a great deal of information such as: particle concentration, rate of change in concentration, composition, particle size and shape, principal metals, etc. It is not economically feasible to monitor all variables. At least one role of the lubrication and wear specialist is to provide guidance in selecting the most appropriate variables to monitor. He must further be involved in the problems of prognosis. How will the wear condition change with continued running, and what condition calls for some action?

THE REDUCTION OF DIRECT operating cost of commercial and military aircraft is becoming an increasingly important thrust for future aircraft design. The use of engine condition monitoring systems has substantial potential in reducing unnecessary maintenance action and improving flight readiness and safety.

Diagnostic systems can monitor engine performance through gas path pressure and temperature measurements and fuel flow measurements. They can also monitor the condition of mechanical systems containing bearings and gears. Corrosion and wear play an important role in failure and component replacement. The objective of this paper is to review the failure modes of aircraft oil wetted parts, particularly in helicopter engines and transmissions, and to highlight some of the health monitoring concepts and diagnostic devices.

The influence of various wear modes in aircraft has impact on safety, performance, and life. Generally performance, as measured by specific fuel consumption (SFC), has not been a critical factor influencing engine scheduled overhaul. However, with increasing fuel costs there is a growing concern over performance retention over the engine life. Presently, fuel cost account for 45% of the operating expenses of domestic wide body aircraft like the 747 and DC-10. Wear activity contributing to performance degradation include erosion of turbine blades and wear of shaft seals and gas path seals. A clearance change of only 1% of blade height affects specific fuel consumption 1.5 to 2%. While SFC is indeed an economic concern, the impact of wear on the cost of unscheduled maintenance and the time between overhaul (TBO) is substantial enough to make complex diagnostic systems worthwhile. This is particularly true for helicopters where the mechanical

and dynamic complexity is much greater than fixed wing aircraft. Here, high speed gas turbine engines drive low speed rotors through light weight high torque transmissions. In addition, helicopters operate over a large number of high temperature cycles and in dirty environments. The TBO for helicopter engines is on the order of 2000 hrs. compared to 10,000 hrs. for fixed wing aircraft. The added mechanical burden of the transmission and drive train make maintenance a more critical issue than performance. According to (1)* the drive system alone accounts for 30% of the direct maintenance costs. The primary purpose of diagnostics of oil wetted parts is to reduce unscheduled maintenance, increase time between overhaul and create an opportunity for "on-condition" maintenance.

ENGINE WEAR MODES

Many of the engine maintenance problems are related to bearings and seals. A study of the T53 and T55 engines (2) shows that 37% of unscheduled maintenance is due to seals. This is generally in the form of carbon wear. Coking also occurs when pressurization air at idle drops causing oil to leak past the carbon seal. Of the oil wetted parts, bearings are the most critical component accounting for 25% of unscheduled repairs. These are followed by gears and splines. Early versions of these engines generated wear particles from outer ring rotation. Wear also occurs between the cage and bearing ring. A more serious problem is associated with roller skewing. This produces particles from roller end wear but it can also cause catastrophic failure of the cage. Most cage failures are too sudden for diagnostics to be effective. The event usually results in total engine failure and possibly forced landing.

Beerbower (3) has listed the relative frequency of various wear modes from the investigation of (4). These include low cycle sliding fatigue, rolling fatigue and abrasive wear. The dominant wear mode was sliding fatigue (54%) which includes roller skidding damage, cage wear and nonclassical spalling due to excessive load or manufacturing errors. Corrosion is not specifically categorized in some studies but in the military it is generally felt that presently it accounts for as much as 30% of bearing removals.

As will be discussed later, debris is a major cause of component wear and deterioration. Airborne debris accelerates compressor and turbine blade erosion. The dirty environments encountered by helicopters has led to the development of inlet particle separators which has improved the mean-time-between-depot-returns (MTBD) for erosion from 3000 hrs. in 1966 to over 100,000 hrs. in 1973 (2). Erosion is now a problem in the separators themselves.

Dirty air from compressor bleed can get into bearing cavities and produce debris damage to bearing surfaces which can lead to surface initiated fatigue. There is also some concern about compressor blade/shroud wear particles entering the bearing cavities.

*Numbers in parentheses designate References at end of paper.

TRANSMISSION WEAR MODES

Studies of transmission failures reveal that bearings are the most sensitive component. Peterson et al. (5) and (6) condensed the data of (7) and showed that the frequency of component malfunction is: bearings 46%, gears 23%, liners 15%, misc. (shaft, clutches, lube system, etc.) 16%. A greater variety of wear modes are present in the transmission than in the engine because of the larger number of gears and their characteristic wear modes. Beerbower (3) has summarized the frequency of wear modes for bearings and gears for two transmissions (UH-1 and CH-47) from the data of (7) and (8). This is shown in table 1. The dominant wear modes as well as the frequency of component malfunction show different patterns for each transmission. This is true for engines as well as transmissions and it continually changes with time as corrective modifications are made. Both transmissions show greater malfunctions with bearings than gears. The UH-1 encounters more abrasion than the CH-47 which is more sensitive to rolling fatigue. Corrosion is common to both.

The studies clearly show that classical fatigue failure of bearings is rarely observed. Bearings are generally removed because of other competing failure modes such as corrosion, debris denting and manufacturing defects (grinding furrows). In addition, the advent of clean bearing materials (vacuum arc remelt and degassing processes) has reduced the probability of classical subsurface initiated fatigue. Bearing life is now seen to be more surface sensitive. Gears tend to be a little more tolerant of surface defects than bearings. They also are a source of debris generation along with other components producing sliding wear or fretting (splines and bearing race/housing interfaces). In general, the wear of gears and splines do not reduce their ability to function. Their wear particles, however, cause secondary damage to other components like bearings which are more sensitive to debris. A transmission research engineer from the U.K. has concluded that "cleanliness is godliness." To avoid secondary and progressive damage due to contaminants a U.S. manufacturer is using a modular transmission design separated by filter screens. The sensitivity of bearings to debris damage and the substantial abrasion mode of wear in transmissions as shown in table 1 has motivated the Army to initiate a program on oil debris analysis and superfine (3 μ m) filtration (9).

DIAGNOSTICS

Condition monitoring procedures involve the three key elements of detection, diagnosis and prognosis. Detection must reveal an abnormality such as excessive wear. Diagnosis further clarifies the abnormality as to what component may be experiencing a malfunction. Prognosis is the act of foretelling the rate of deterioration and when corrective action should be taken.

Of the many detector methods that are available there seems to be three general statements that can be made. First, the concepts used in the various detection devices are generally complimentary. Second, the deficiencies encountered in the field are being corrected through improved designs. Third, the success of the diagnostic device can only be achieved if it is sensitive to the critical failure modes of the mechanical system.

There are two general classes of detection methods for oil wetted parts: vibration or vibration related (such as shock pulse) and oil (or particle) analysis. Vibration related methods are attractive because they are simple, inexpensive and not affected by filtration level or the use of grease rather than oil. Oil analysis, however, is more sensitive to wear and will be considered in more detail here.

Lubricating oil, in addition to acting as a lubricant and coolant, carries with it information that it has collected by way of wear particles or oxidation products as it journeys through the oil wetted parts. The concept of oil analysis is based on the premise that the type of wear or debris particles, if collected and analyzed, is indicative of the wear and surface condition of the internal components. Sampling alone presents substantial problems due to: settling of particles, adhesion to component walls, filtration and other factors affecting consistent, timely and useable samples. Once a debris sample is obtained there is a great deal of information (generally more than practicable) that can be obtained from them. These can be characterized by: concentration of particles, rate of change of concentration, dominant metals present, distribution of various metals, particle size distribution, particle shape and chemical form (e.g., metal, oxide, metallo-organic). Despite the difficulties in sampling and the limited range of particle sizes that detection devices operate in, the various oil monitoring techniques have been relatively successful. Some of these techniques are briefly described below.

SOAP - Spectrometric oil analysis program (SOAP) is widely known and has been used for many years in the U.S., U.K. and Canada. Periodic oil samples are taken from engines or transmissions. These are examined spectrographically for metal type and concentration. The method is sensitive to particles smaller than 10 μ m. It has limited ability to isolate faults. The general feeling in the military is that SOAP is approximately 80% effective in isolating engine failures and perhaps a little less effective with transmissions (3). A factor influencing the lack of SOAP success is the time involved in the logistics of sampling, shipment and laboratory analysis. Some aircraft require a SOAP analysis after every flight. There is currently interest in developing a portable SOAP analyzer which can be taken on-board.

CHIP DETECTORS - Chip detectors are used extensively in helicopter engines and transmissions. The contain a magnet and are positioned in the oil system to collect ferrous debris for periodic inspection and trend monitoring. Chip detectors are most effective in collecting large particles (25 μ m to over 500 μ m) that may come from fatigue spalls. Experience seems to indicate that more failures are accompanied by relatively large particles (>50 μ m). For this reason chip detectors compliment SOAP which can more appropriately monitor the smaller particles and normal wear conditions.

Chip detectors can give on-board fault indication. Metal particles which bridge the gap between two electrodes in the chip detector activate a warning light. It is well known that there are a large number of false indications with these devices (many chip lights have been disconnected). The warning light will go on regardless of whether the gap is bridged by a large number of small particles, a small number of large particles or a single long narrow particle. This problem has been effectively resolved by the use of a capacitive discharge burnoff chip detector (10). When the gap between the electrodes is bridged a strong current pulse from a capacitor is discharged which causes local melting of the fine particles ("fuzz") that cause false readings. Larger particles will continue to bridge the gap giving a true reading. These types of detectors used in a full-flow-through mode within the oil system appear to be quite promising.

FERROGRAPHY - Ferrography is a more recent development (11). A small sample of oil is allowed to flow over a glass slide located over a high gradient magnet. Magnetic particles such as iron and iron oxide are precipitated out with the larger particles located at the entry point. The particle size range is on the order 0-20 μ m. The prepared slide can be examined

under a special microscope using bichromatic illumination which reveals metal in red and oxide in green or yellow. Further analysis can be done with the scanning electron microscope and other surface analytical tools to determine chemical and elemental content (12). This is an excellent laboratory tool which can distinguish between various particle morphology and wear modes. It is called an Analytical Ferrograph.

A simplified version, known as the Direct Reading Ferrograph, uses optical density measurements to determine the amount of wear. A more recent version, the Real-Time Ferrograph, was developed for on-board monitoring.

IN-LINE OIL MONITOR - A technique which has had some success in engine condition monitoring of oil wetted parts employs the principles of light scattering for particulate debris detection and light attenuation for chemical and thermal degradation (13). This system has been tested in the TF41-A-2 engine as part of a total inflight engine condition monitoring system (14). It provides greater information than some other on-board systems and is effective over a large range of particle sizes, but appears to be quite expensive.

RADIOACTIVE ISOTOPE TAGGING - This method is not frequently used but is very effective in isolating faults in critical components. One example of its use has been to monitor cage wear of an engine bearing (2). A silver isotope layer is deposited below the normal silver plating. When the silver wears beyond a critical level the silver isotope is released into the oil system and detected by a Geiger Mueller counter. This method is also being used to monitor the roller end wear of a critical main shaft engine bearing of a military engine.

EFFECT OF FILTRATION

There is evidence that an ultra clean oil system can increase bearing life considerably through a reduction of debris damaging surface stress raisers (15). The quantitative effect of improved filtration on life is not clearly documented, but the trend is certainly there (16). At least the appearance of bearing surfaces and the amount of sludge has improved with finer filtration (9).

Filtration down to the 3 μ m level removes most of the particle information used in many oil monitoring methods (17) and periodic oil sampling becomes ineffective. Alternative measures must then be taken. These could include continuous on-line monitoring upstream of the filter or a system which incorporates the filter as part of the detection device.

PROGNOSIS

Good diagnosis is helpful to prognosis which involves the prediction of residual life or function of a component based on the wear trend and mode that has been observed. Many components, when considered failed, have been preceded by a progression of deterioration due to wear over a period of time. This is the basic premise of diagnostics through particle analysis. Beerbower (3), using his model for various wear modes has predicted qualitatively the rate of accumulated wear with time. Sliding fatigue wear and corrosive wear proceed rather slowly with time. The rate of abrasive wear and particularly scuffing wear increases with time and occurs more rapidly. Rolling fatigue wear occurs quite rapidly with not a great deal of advanced warning once a fatigue spall is formed. Even then safe operation may still be available for hundreds of hours.

Future mechanical components may be characterized by different wear modes or at least a different distribution of wear modes. This could occur as the result

of surface treatments (for debris tolerance), new lubrication concepts and operation in different regimes of severity. As an example, advanced engines are proposed that operate at much higher speeds which with currently used materials, can cause catastrophic fracture of bearing rings as the result of crack propagation from a surface fatigue spall.

CONCLUSIONS AND FINAL COMMENTS

1. The use of appropriate diagnostic tools for aircraft oil wetted components has good payoff in the reduction of direct operating costs through reduced unscheduled maintenance. Diagnostics is a means by which the practice of regularly scheduled maintenance can be transformed into on-condition maintenance.

2. Diagnostics is particularly important in helicopter engine and transmission systems where reliability of oil wetted parts are a significant factor in direct operating costs. Bearings account for the majority of failures. They are more sensitive to secondary damage from debris than gears.

3. There are several useful diagnostic methods for oil or wear particle analysis. They are generally effective over a limited range of particle sizes but tend to compliment each other if used in parallel.

4. Fine filtration (<40 μ m) has the potential of increasing time between overhaul, but reduces the effectiveness of oil monitoring techniques if conventional sampling methods are used. Alternative diagnostic techniques or at least sampling methods, must be used. Further diagnostic modifications may have to be considered for future aeronautical systems which may incorporate more grease lubrication, self-lubricating materials, sealed-for-life components and mist lubrication.

5. The development of a diagnostic system should be parallel and integral with the development of a mechanical system. Diagnostic measurements must accompany bench tests of components for ultimate reliability and effectiveness of both.

6. A diagnostic technique like ferrography has benefitted the science of tribology as much as the science of tribology has helped it become an excellent diagnostic tool. Greater collaboration between designers of mechanical systems, designers of diagnostic systems and tribologists would be beneficial.

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Table 1. - Relative Frequency (%) of Wear Modes
in UH-1 and CH-47 Transmissions

Wear Mode	UH-1		CH-47	
	Bearings	Gears	Bearings	Gears
Sliding fatigue ^a	0	19.01	5.97	8.24
Rolling fatigue ^b	14.12	1.95	29.08	0
Adhesive	0	11.72	4.55	4.82
Corrosion	20.99	2.48	25.80	9.46
Abrasion	22.19	3.27	2.74	0.64
Fretting	<u>4.27</u>	<u>0</u>	<u>1.89</u>	<u>6.81</u>
Total	61.57	38.43	70.03	29.97

^aLow cycle.

^bHigh cycle.

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Ordinarily one thinks of Technology Transfer as the application of basic scientific principles to an engineering or technological process. This implies that the subject is well understood but that application has not yet taken place. In the present context, such is not the case. Here we mean that basic principles and mechanisms are known in physics and chemistry, but that these have not yet been successfully applied to the fundamental processes of wear and corrosion. When this endeavor proves successful, the theories of the mechanisms of wear and corrosion can then be applied to engineering and industrial processes, the next phase of Technology Transfer.

Wear is a particularly striking and technologically important manifestation of the coupling of mechanical energy to chemical energy, extremely rich in physical and chemical mechanisms. While this richness and the ensuing complexity provide a fertile ground for life-long investigations of various facets of wear, it also creates the impression that to search for a unifying picture in terms of a few governing fundamental quantities would be futile. Worse, this complexity creates a feeling that even if such a construct is found, the path from these laws and principles to technological applications would be a very long one, most probably hopelessly tortuous, and might not even exist. We argue here that such impressions are erroneous, and in support of our thesis we shall give the highlights of a theory, details of which can be found in recent publications. (1-5)

We mentioned that chemistry plays a major role in wear; much of the chemistry involved has been referred to in the now popular phrase "environmental effect." Thus, one comes across quite a number of articles about "the effect of environment on mechanical properties of materials." However this concept in its fundamental form goes as far back as the work of Gouy⁽⁶⁾ in the context of electrochemistry. This was done in the latter part of the last century. While in the context of the mechanical strength of solids, it goes back to the works of Joffe⁽⁷⁾ and Rebinder⁽⁸⁾ in the 1920's.

We shall only briefly touch upon the highlights of their works, of the more recent investigations of Westwood and his collaborators, and the very recent work of ours⁽¹⁻⁵⁾ which we believe ties all these investigations into a coherent picture. This cohesiveness arises from the realization that a single fundamental quantity, a single driving force, namely the gradient of the chemical potential of certain atomic-molecular species, is the fundamental quantity. The chemical potential of the specific species is in turn dependant on the environment—which may be an electrolyte, a solid with defects, or a combination of these. Tracing the time evolution of the chemical potential enables us to identify and decode the intricate processes such as adsorption and diffusion that take place. This ultimately leads to breaking of bonds and separation of solid material from the main solid body—namely wear. One of our objectives is to indicate that the above ideas, due to the very richness of the wear processes, bear on a large number of technological applications going beyond simply the wear of mechanical components of drilling of rocks, and embrace such diverse phenomena as crack propagation, hydrogen

embrittlement, and the very process of adhesion, to name a few.

Gouy had made the observation that the surface tension in contact with electrolytes could be changed drastically by minute amounts of additives in the electrolyte solution. Note, moreover, that surface tension is nothing more than free energy per unit surface area. Even though this fundamental connection to the Helmholtz free energy—which is also interpretable as the mechanical energy available to do useful work—does exist; the connection to the Rebinder effect that will be described now must have seemed rather remote for a long time because otherwise this connection would have been used to arrive at a better understanding of wear before now. As we shall see, up to now there has been a missing link, the chemostress effect.⁽³⁾

Having discussed the Guoy effect we come now to the Rebinder effect, which different groups interpret in different ways.

Although generalizations of this effect have been noted, for our discussion it is sufficient to say that it is the dramatic change observed in the microhardness of a solid when minute amounts of additives are added into the "lubricant" used between the indenter and the solid.

Rebinder's original explanation of this effect was that it was related to a change in the surface free energy. This is a natural connection to be made if we remind ourselves of Rebinder's insistence that the effect was for very small loads, in the elastic reversible regime.

Of course, observation of this effect in the elastic regime does not necessarily preclude its existence and observation in the inelastic irreversible regime and indeed, this latter also has been observed. It too is called "the Rebinder effect" and investigated at length by Westwood, McMillan, Latanision, their collaborators,⁽⁹⁾ and Cuthrell and collaborators.⁽¹⁰⁾

If one focuses on the mechanisms involved, it is clear that distinction is not just a matter of semantics. It is immediately seen that to pass to the inelastic regime to obtain permanent indentations, the formation and dynamics of defects such as dislocations, slip mechanisms, etc., will be involved. These structures will have to penetrate well below the ideal perfect crystal "surfaces." This is so, since consideration of the range of the surface forces involved would limit the effective surface of the solid to only a few atomic layers into the bulk.

In fact, it is precisely at this point that the main dilemma arises: if surface forces have such a short range into the bulk, why should what is added to the lubricant in minute amounts have anything to do with what happens in the bulk where inelastic generalized Rebinder effects are observed? Again, we are reminded of the significant observation of Westwood and coworkers, shown in Fig. 1, that there are correlations between the value of the zeta potential, the hardness of the solid, and the drilling rate. If we had only the elastic Rebinder effect, one could invoke the Guoy observation and the matter would be closed.

To resolve the dilemma one needs to pinpoint specifically to some fundamental quantity, some fundamental mechanisms that also involve changes in the bulk properties of the solid. The obvious mechanism that has been ignored is the diffusion of specific ions. This diffusion is in turn affected by stress fields,

temperature gradients, and defect structures in the material. The driving force of the diffusion is the gradient of the chemical potential μ which is affected by stress fields σ according to the following relationship:

$$\frac{\partial \mu}{\partial x} = \frac{\partial \mu}{\partial \sigma} \cdot \frac{\partial \sigma}{\partial x} + \dots$$

where $\frac{\partial \mu}{\partial \sigma}$ has been calculated⁽¹⁻⁵⁾ and has been designated as the chemostress coefficient.

The importance of diffusion in the context of oxidation has already been pointed out by Wagner in his theory of oxidation.⁽¹¹⁾ The dependence of the chemical potential on stress is necessary in a quantitative description of oxidation and corrosion under stress. So it is in this connection that our discussion presented here touches on the basic relationship between chemistry and wear.

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TECHNOLOGY DEVELOPMENT AND NATIONAL STRENGTHS

Hans Mark, Acting Secretary of the Air Force

LADIES AND GENTLEMEN. I am particularly pleased to be here today to have the opportunity to talk with this group. I come from the scientific community myself and know something about your problems. However, with your permission I would like to talk about some problems of my own and I hope that what I have to say would be of interest to you because I believe these problems are ones that we share in common.

It has become very fashionable among some in Washington to doubt the ability of this country to continue to be a world power. This view is held by many people who have influential positions, both in public and in private life. It is by no means a majority view, but one that is significant in that it is held by people who are in positions that tend to set the nation's intellectual goals.

People who hold this view tend to make two arguments: One is that they question the propriety of the United States playing a major role in world affairs in that they are not sure that this country can be trusted to use its power and wealth with wisdom and restraint. Others question the fact that we can, in fact, physically maintain a strong position at all, what with the various economic and social problems that seem to beset us. I would like to examine some of these questions here today to see what, if anything, that is useful might be said about them.

First and foremost let me start by saying there is no doubt whatsoever in my mind that the United States will continue to be a major power in the world almost independent of what some of our leading citizens think. We have some very important permanent strengths that would have to be reckoned with as a force in the world even if the nation's leadership decided not to push the role of the United States as a world power. These permanent strengths are a result of our geographic position and of some very deeply rooted, political and economic history.

First, there should be no question at all in anyone's mind regarding our position in agriculture. We are the world's leading agricultural nation. It is interesting to see, if you look at the map, why this is the case. We are the largest country in the world lying entirely within the temperate zone. This is the region in which agriculture can be carried out on a mass scale. Canada and the Soviet Union are too far north to do this properly. The Soviet Union, for example, has a southernmost point which is at the same latitude as San Francisco, California, and the parallel going through Moscow, their capital, also goes through Ketchikan, Alaska. Other large nations lie in the tropics and this position presents peculiar problems of its own with respect to carrying out large scale agricultural activities. Not only can we feed ourselves but we can feed a large part of the world and we can do all of this with less than five percent of our population. Clearly this is a major strength which we have

used on occasion to enhance our international position by conducting major famine relief operations as we did in the Sahel a few years ago or by using grain import permits to the Soviet Union as a lever to achieve certain political objectives.

Our strength in agriculture is deeply rooted in our political and social traditions. The Homestead Acts which have been passed by successive Congresses throughout our entire history go back to the Northwest Ordinance of 1787 which was the first measure designed to encourage people to move west and to develop the land. Perhaps the most famous Homestead Act of all was the one passed in 1862 which was essentially a veteran's benefit measure for people then fighting in the Civil War. In addition to making free land available to people under certain conditions, it established the Land Grant Colleges. I think a good case can be made that the establishment of these institutions was perhaps the single most influential and far reaching measure ever passed by the Congress. The full intent of the law is perhaps worth quoting verbatim since it led directly to the second great strength we have as a nation, which is the development and application of new technology.

In the words of the ACT it was intended to provide for the support "of at least one college (in each State) where the leading object shall be, without excluding other scientific and classical studies and including military tactics, to teach such branches of learning as are related to agriculture and the mechanic arts, in such a manner as the Legislatures of the States may respectively prescribe, in order to promote the liberal and practical education of the industrial classes in the several pursuits and professions of life."

You all know that mechanic arts in those days meant technology development and engineering and therefore these institutions began to produce a large number of knowledgeable people in these fields. You also know that in 1887, the Homestead Act of 1862 was amended to establish "agricultural experiment stations and engineering experiment stations" at each of these institutions. These research establishments are now at the very heart of our public education system and they produce to this day the large majority of agricultural people and about fifty percent of our engineers.

The art of taking scientific discoveries and turning them to practical ends is something that we do peculiarly well in this country. Alexis de Toqueville, writing in 1840 in his famous and perceptive book "Democracy in America" has a chapter entitled "Why the Americans Are More Addicted to Practical than to Theoretical Science". He said, "In America, the purely practical part of science is admirably understood and careful attention is paid to the theoretical portion which is immediately requisite to application. On this head the Americans always display a clear, free, original and inventive power of mind." I think what de Toqueville saw 130 years ago is still true today. It is remarkable how many of the modern technological achievements originated in this country. I need not make a list here but you certainly all know what they are. All you have to do is look around and see the enormous number of inventions that have made life both easier and more interesting for all of us.

It is entirely appropriate that I should be talking to this group about these things because in a very real sense, you, the people sitting in this room, are the custodians of these great national strengths. Our scientific research establishments, in particular and our institutions of higher education more generally are still the major sources of people who propagate these

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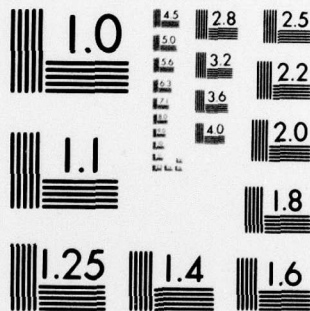
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traditions. It is a great intellectual tradition in this country which must be nurtured and preserved and I know that you will do just that.

A discussion such as this one would not be complete if I did not also mention our major weakness which is, I believe, a temporary one. This weakness is, of course, our current dependence on imported oil. There is no doubt in my mind that in the next decade we shall have to develop our internal energy resources in such a way that we will achieve virtual independence of foreign oil sources. I know that can be recovered by secondary and tertiary recovery techniques. We also have plenty of nuclear fuels. All of these resources will have to be developed and we will have to make the capital investments and the economic sacrifices that will go with this development. Fortunately, we are strong in the creation of new technology and this is, of course, precisely what the development I speak of will require. We have the ingenuity, imagination and skill to overcome the difficulties we face in achieving energy independence and I expect that people who are now working in some of the organizations you represent will take a leading role in this most important effort.

We are told by many of our political leaders that we face an era of limits. Perhaps this is so, but I think we need to remember that even though we always face physical limits the human imagination is not limited. It is precisely by using and developing our imaginations that each generation has transcended the limits perceived by the preceding one. It is most important in my opinion to remember this point and it is especially important for you since scientific research is one of the major activities that stimulates the imagination of the next generation.

Thank you very much.

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